THE JOURNAL

OF THE

AMERICAN CERAMIC SOCIETY

NOVEMBER 1, 1945

MONTHLY PUBLICATION DEVOTED TO THE ARTS AND SCIENCES RELATED TO THE SILICATE INDUSTRIES

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Publication Office: 20th & Northampton Sts., Easton, Pa.
Editorial Office: 2525 N. High St., Columbus 2, Ohio
Committee on Publications: R. L. Stone, *Chairman:* Harry Thiemecke, W. A. Weldon, K. C. Lyon, and R. C. Purdy, *ex officio*

Entered as second-class matter at the post office at Easton, Pa., under the act of March 3, 1879. Published monthly.
Subscription fifteen dollars ($15.00) a year. Single numbers $1.50
(Foreign and Canadian postage, 50c additional on subscriptions)
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THE JOURNAL
OF
THE AMERICAN CERAMIC SOCIETY

Vol. 28 November 1, 1945 No. 11

GLASS DENSITIES BY SETTLING METHOD*

Water-Bath Apparatus for Production Control in Glass Plants

By Mellen A. Knight

Abstract

A simplified sink-float apparatus and method for measuring the densities of lumps of glass are described. Several lumps, of approximately two grams weight, of unknown density and one lump of glass of known density are placed in a heavy-liquids mixture contained in a test tube. The tube is immersed in a water bath that is heated automatically at a uniform rate; as the lumps settle, the temperature is noted at which each lump passes a reference line marked on the tube. The density of each unknown may be expressed simply in terms of the difference between its temperature and that for the standard lump, or these temperature differences can be converted to density differences or to absolute densities. The precision (reproducibility) of the measurements is represented by a standard deviation of approximately ±0.0001 gm. per cc.

The method is rapid and convenient and requires a minimum of training of the operator. It is believed to be more practical for plant laboratories than the other available methods. It is especially applicable to measurement of daily densities for production control in glass plants and to trouble-shooting investigations of composition heterogeneities; large numbers of samples can be tested rapidly and precisely. Complete information as to sampling, operation, and calculations is given.

I. Introduction

Density measurements made by a variety of methods have been used in glass plants for some years. Some of the most valuable of these methods have involved various adaptations of the sink-float principle utilizing mixtures of heavy liquids. Several of the methods have been discussed in the technical literature.[1] These density measurements have proved to be very useful in the control of glass and ware quality during production, and the recent developments in the use of statistical methods in production control have found especially valuable applications with daily density values.[2] These new applications emphasize the need for rapid and reliable methods for the measurement of the densities of lumps of glass. The method described herein fulfills these requirements and appears to be the most satisfactory of the available techniques. It is rapid and precise and requires a minimum of apparatus and special training on the part of the operator.

The present method involves the settling of lumps of glass in a mixture of heavy liquids; this is done in a

*Forty-Seventh Annual Meeting Program, The American Ceramic Society (Glass Division, No. 13). Received June 16, 1945. This paper constitutes a report of one of the researches sponsored by the Glass Container Association of America in the year 1944.

[1] (*a*) A. R. Payne, "Density Control of Glass Tanks," *Glass Ind.*, **9** [6] 121–25 (1928); *Ceram. Abs.*, **7** [8] 529 (1928).

(*b*) A. R. Payne, "Elementary Laboratory Method for Determination of Density of Glass," *Glass Ind.*, **9** [9] 191–94 (1928); *Ceram. Abs.*, **7** [11] 748 (1928).

(*c*) G. W. Morey, Properties of Glass, pp. 223–26. Amer. Chem. Soc. Monograph Series, Reinhold Publishing Corp., New York, 1938. 561 pp.; *Ceram. Abs.*, **18** [2] 48–49 (1939).

(*d*) J. C. Turnbull, "Separation of Inhomogeneities in Bottle Glass by Density Differences," *Jour. Amer. Ceram. Soc.*, **24** [2] 37–43 (1941).

(*e*) J. C. Turnbull and L. G. Ghering, "Cord Analysis," *ibid.*, **24** [8] 264–70 (1941).

(*f*) "Glass Composition Control by Use of Specific-Gravity Determinations," *Glass Ind.*, **22** [9] 384–86 (1941); *Ceram. Abs.*, **21** [1] 8 (1942).

(*g*) T. C. Vaughan, "Determination of Density by Flotation Method," *Bull. Amer. Ceram. Soc.*, **23** [2] 68–69 (1944).

(*h*) L. G. Ghering and M. A. Knight, "Properties and Diagnosis of Cords in Pressed and Blown Glassware," *Jour. Amer. Ceram. Soc.*, **27** [9] 260–66 (1944).

(*i*) M. A. Knight, "Calculation of Density and Specific-Gravity Data for Container Glasses, Corrections for Temperature and Air Buoyancy," *Glass Ind.*, **26** [4] 173–75, 198–99 (1945).

[2] L. G. Ghering, "Refined Method of Control of Cordiness and Workability of Glass During Production: Statistical Control Charts Applied to Daily Measurements of Density," *Jour. Amer. Ceram. Soc.*, **27** [12] 373–89 (1944).

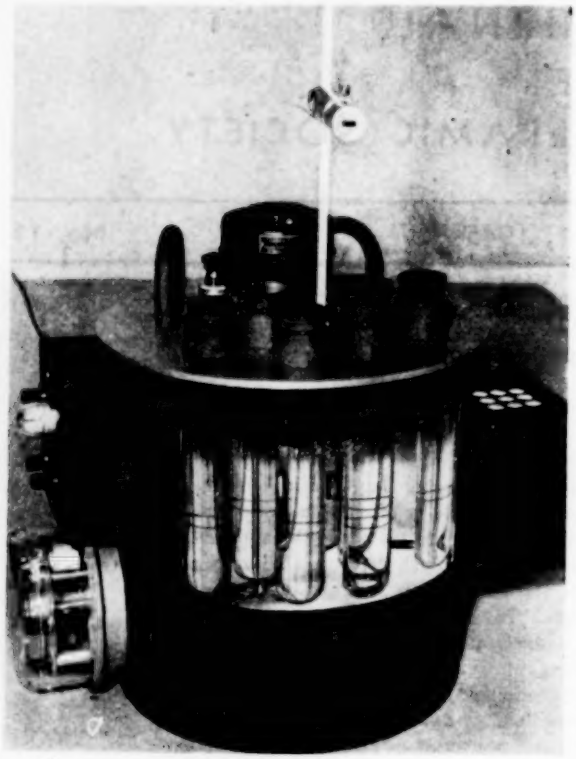

Fig. 1.—Front view of settling bath; a revised design allows all six sample tubes to be viewed at once.

water bath by means of constant heating of the liquid.* The temperatures are read at which the unknowns and a lump of standard glass settle past a reference level in a tube of heavy liquid. The densities of the unknowns are then calculated from that of the standard by means of the predetermined coefficients for the changes of density with temperature for the liquid and for the glass.

II. Apparatus

(1) Temperature Control

There are three kinds of temperature schedules that can be used in this type of water bath for the determination of lump densities; the equipment that is required depends on the kind of schedule used: (*a*) The bath can be heated at a steady rate and the temperatures recorded at which the lumps settle past a reference level in the tube; (*b*) the bath can be cooled at a steady rate with the temperatures being read at which the lumps rise past the reference line, or (*c*) the lumps can be balanced at constant temperatures, the bath temperature being controlled by a thermoregulator system. Of these possible methods, (*a*), that of steady heating, has been found to be most satisfactory; it gives reproducible results, quickly and efficiently, and requires a minimum of apparatus. This method has the advantage over the second, (*b*), in that heat input can be more accurately and easily controlled than can cooling. The last method, (*c*), involving balancing of the lumps at constant temperatures, is very tedious, and it yields no further accuracy over the other two methods. Density values on various test lumps determined by balancing at constant temperatures, both in the water bath and in the stroboscopic centrifuge, agree with values found by method (*a*) within the precision of measurement. Method (*c*) also requires a sensitive thermoregulator system that adds to the expense and the complexity of the apparatus.

It is not necessary that the heating rate be exactly constant throughout all the temperature ranges over which the bath may be used; a reproducible heating schedule is the prime requisite. A power input such that the bath is heated uniformly at about 0.1°C. per minute gives satisfactory results. This can be realized very simply by manual, on-off, control of the heater. The precision of control and ease of operation of the bath, however, are greatly enhanced by the use of an automatic, time-clock regulator to control the on-and-off periods for the heater.

The temperature distribution among the various tubes of liquid holds very nearly constant during any particular run, the temperature in each sample tube increasing at the same rate as that in the thermometer tube. Since the temperature differences between the tubes vary somewhat between runs, it is necessary to use a standard lump in each tube on every run. In this way, each tube is calibrated for the whole of each run.

(2) Description of Apparatus

The water-bath equipment forms a self-contained unit weighing about 25 lb. exclusive of the water; it can be set up easily wherever cold water and 110 volts a.c. are available. A view of the equipment is shown in the photograph of Fig. 1. The sketch of Fig. 2 gives the essential features of the design of the bath. The water vessel, *A*, of Fig. 2, consists of a cylindrical Pyrex-brand glass jar, 10 in. in diameter and 10 in. high. This glass vessel rests in a tank, *B*, made of 14-gauge galvanized steel; the inside of the tank is painted white to increase its reflectance. A window cut in the front of the tank permits viewing the six sample tubes, *C*. A 25-watt lamp with a diffusing screen is mounted in a housing, *D*, on the side of the tank for illuminating the bath. Thus a uniform illumination is obtained, and the bath is shielded from stray rays of sunshine that upset the temperature distribution in the bath.

The aluminum lid, *F*, covers the bath and supports the sample tubes, *C*, the stirrer, *G*, the thermometer, *H*, the electric heater, *E*, and the copper cooling coil, *J*. Each sample tube is suspended directly through a hole in the lid by means of a rubber collar, *K*. The tubes are 32 mm. in diameter and 200 mm. long, each having a reference line 2 in. above its base. They are filled with liquid to a depth of $4^1/_2$ in. and kept stoppered except when samples are being added or removed. Constant and rapid circulation of the water is maintained by the stirrer so that the temperature distribution in the bath

* When powdered samples have to be tested, the stroboscopic-centrifuge technique is required (see footnotes 1 (*d*) and 1 (*e*); the density distribution of powdered samples cannot be determined in a simple water bath.

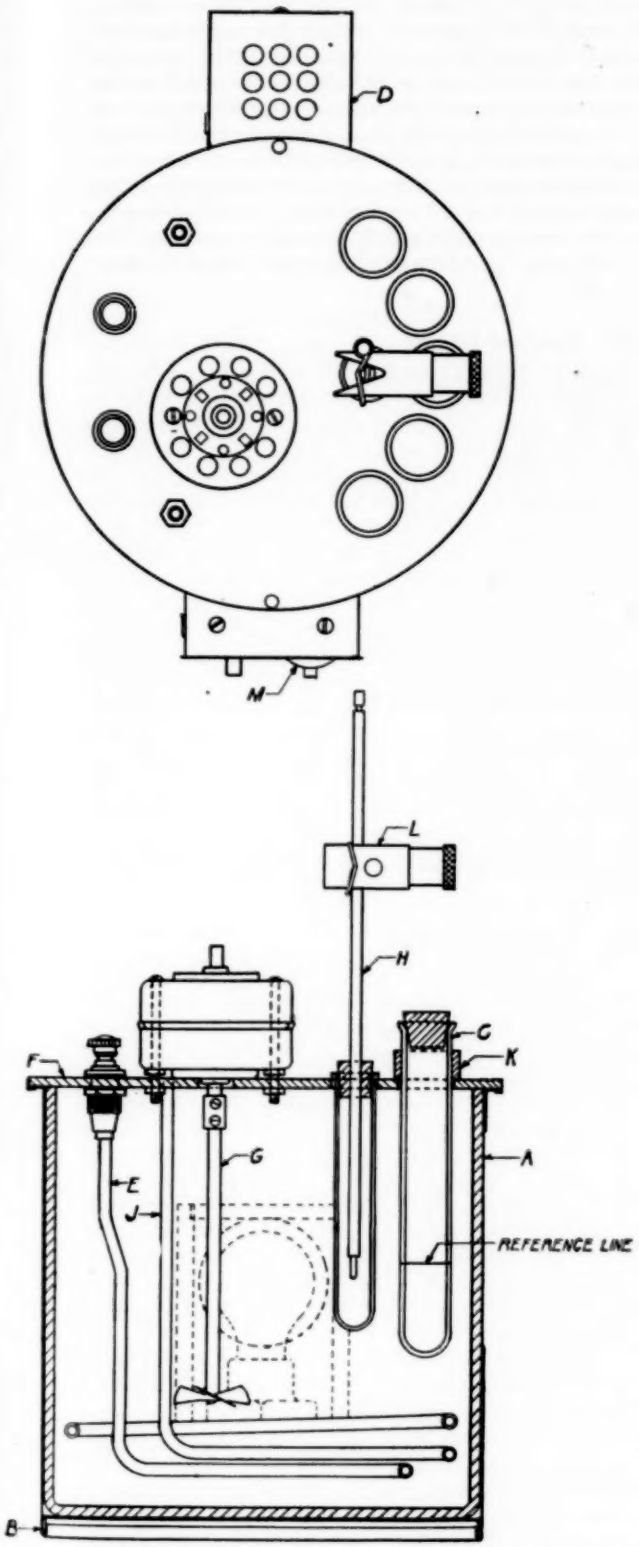

Fig. 2.—Diagrammatic sketch of apparatus; only five sample tubes are shown; the new bath is equipped with six tubes which are nearer to the thermometer.

remains constant throughout the test. The thermometer, immersed in a seventh tube of the heavy-liquids mixture, is graduated in 0.10° divisions from −10° to 50°C. The meniscus magnifier, *L*, permits estimation of temperatures to hundredths of a degree.

The heating ate for the bath is regulated by means of the relative on-and-off periods for the 300-watt copper heating coil, *E*. These periods are controlled by the time clock, *M*, by which the percentage of "on" time can be adjusted. For example, with the equipment described above, the heater is turned on for the first 12 seconds of each minute in order to realize a 0.1°C. per minute heating rate. The exact period that is required is affected by the room temperature and by the particular temperature range involved. To bring the bath to the desired temperature before a run, the cooling coil or the heater can be used as needed, with manual control.

(3) Heavy Liquids

Various pairs of organic liquids have been used in sink-float work reported in the literature. The liquids in use in this laboratory are α-bromonaphthalene and *s*-tetrabromoethane. Mixtures of these liquids having densities in the range of 2.4 to 2.6 gm. per cc. will change in density by −0.00178 gm. per cc. for each 1°C. increase in temperature. For the commercial "soda-lime-silica" glasses (having coefficients of cubical expansion between about 2.6 and 3.0×10^{-5} per °C. and densities between 2.4 and 2.6 gm. per cc.), the temperature coefficient to be used in the calculations is −0.00171 gm. per cc. per °C., that is, the difference between the coefficient for the liquid and that for the glass. For use with low-expansion borosilicate glasses, the net coefficient is −0.00174 gm. per cc. per °C. These calculations are discussed in detail in section IV. If other pairs of liquids are to be used, the appropriate factors for them must be determined independently.

The mixtures of the liquids have to be filtered periodically to remove accumulated dirt and moisture. Eventually, redistilling of the liquid under vacuum may be necessary. This can be done easily with a laboratory vacuum pump and an oil bath for heating the distilling flask.

III. Experimental Methods

(1) Sampling

The test samples should represent typical ware of good commercial annealing. The ware is to be taken at the same times each day from the same position in the lehr; if practicable, the ware should be from a heavy-pull shop that is near the center of the furnace where pull from day to day is uniform. Each piece of ware is selected to be of some standard grade of annealing; this annealing must be checked on that part of the ware from which the samples are to be taken. This choosing of ware of the specified degree of annealing assures uniform enough heat-treatment so that special reannealing of the samples is not necessary. For example, when bottles are being tested, the test pieces can be broken from the bases of bottles that have been found to have

the same temper number. This is determined on bottles having approximately the same basal thickness by comparison in the polariscope with the standard disks.* The variations in density between bottles of tempers 1 and 2, due to the differences in annealing, will not be greater than about ±0.0002 gm. per cc.; these are by no means large enough to interfere in the analysis of the data. Although carefully controlled reannealing of the test lumps might appear theoretically desirable, it is not only time consuming and costly in every case, but it is also entirely impractical in many plant setups. It is not recommended for commercial practice; controlled selection of the samples makes it unnecessary.

(2) Test Lumps

The test lumps are always broken from the same part of each piece of ware, the annealing having been tested on the part in question. They must be free from cracks, stones, and seeds; cleanly broken surfaces are preferable to sawed ones. In cases of commercially good, relatively homogeneous ware, any lump from the area selected for sampling will represent the ware well. Cordy ware offers special problems, and several lumps may need to be taken in order to represent the variations in the ware. For example, a set of five pieces, weighing from $1^1/_2$ to $2^1/_2$ gm. each, may be taken from the base of a bottle. The lumps can be taken either at regular spacings or from "typical" areas as shown under the polariscope. It is desirable to have the lumps as large as the size of the sample tubes will permit; this is not so important in the case of very homogenous ware but becomes increasingly so as the ware becomes more cordy. Pieces $^3/_8$ to $^5/_8$ in. square may be taken from glass that is from $^1/_8$ to $^3/_8$ in. thick.

If each set of lumps is to be run in a separate tube, the pieces do not need to be of special shapes. When the ware is homogeneous enough so that one or two lumps will give a representative value, the various lumps can be broken to distinctive shapes so that three to five lumps from different samples of ware can be run in one tube; this allows identification of the different lumps during the run.

The average density of the pieces selected should give a representative bulk density for the ware. If the density spread between the lumps is greater than about 0.0010 gm. per cc., the glass is unusually heterogeneous; in extreme cases, a spread of around 0.0050 gm. per cc. is possible between 1-gm. lumps. In these instances, it is very difficult to obtain a representative density by any method, including the Archimedes method where as much as 25 gm. of sample can be used. Since the glass is obviously out of control in such circumstances, no quantitative measurement is needed to confirm this. Hence, this experimental uncertainty offers no problem as far as the plant control is concerned.

These density spreads depend considerably on the distribution of the heterogeneities in the ware. Sets of lumps taken from pieces of ware having the same composition heterogeneity in the glass may differ decidedly in their density spreads. When the heterogeneity is widely distributed in layers parallel to the surfaces of the ware, the spread for the set will be much less than when the heterogeneity is concentrated into local cords.

The ware can be kept clean and grease-free by careful and immediate transfer from the lehr to the laboratory, and clean lumps can then be broken from the ware. These must not be touched by hand and should be handled with forceps at all times. If cleaning should be needed, it is done by scrubbing with absorbent cotton in methyl alcohol.

(3) Standard Lumps

Special glasses of appropriate densities may be used as standard lumps; they may be chosen so as to be distinctive as to color as well as to size. A more common plant practice, however, is to select from current production a piece of homogeneous glass of the correct composition and to keep it as the standard for that glass. In this case, the standard should be broken to an especially distinctive size that will prevent confusion with any of the unknown lumps. It is convenient to use a standard differing from the unknowns by about 0.0010 to 0.0020 gm. per cc. (0.6 to 1.2°C.) in density.

The standard lumps may be calibrated as to absolute density by independent means if such is desired. In some work, only deviations from the usual density are of interest, and the absolute density, as such, is of no special significance. In these instances, separate calibration is not required as long as the same lump is used as the standard. However, a calibration allows interchange of standards in a particular plant and also permits exchange of density values between various laboratories.

(4) Procedure of Run

Several lumps may be run in each tube as long as they can be distinguished from each other and as long as they are of densities similar enough to be tested together efficiently. It is convenient to maintain one or more tubes of liquid suitable for each glass composition as long as that glass is being produced. The composition of the mixture of liquids in each tube is adjusted so that the lumps to be run in that tube will settle at around 27° to 32°C. After the mixture is once adjusted, it need not be altered during its use with glass of the respective composition other than by periodic filtering to clean it. When the samples have been added to each tube, the tubes are stoppered. The appropriate standard lumps should be kept in each tube as long as its respective glass is being made.

At the start of the actual run, the temperature of the bath is adjusted to about one degree below the temperature at which the first lumps are expected to settle, as based on previous runs. By manual control, the full capacity of the heating coil can be used for this purpose. By means of the time clock, the bath temperature is raised at about 0.1°C. per minute until all lumps, both unknowns and standards, have settled to the bottom of the tubes. About once a minute each tube is shaken sufficiently so that its lumps are jarred free from the

* For explanation of temper gradings, see Standard Method of Polariscopic Examination of Glass Containers, A.S.T.M. Designation C148–43. A.S.T.M. Standards, Part II, pp. 362–64 (1944).

surface of the liquid and free from each other. Interference between lumps must be avoided at all times by means of jarring and twisting of the tube. As each lump settles past the reference line on its tube, the temperature in the thermometer tube is read to the nearest hundredth of a degree. On each run, the reference temperatures for the standard and all the unknowns must be measured in each tube; this is necessary because each standard lump settles at different temperatures on successive runs. The data on each tube are then treated as a unit in the calculations, as discussed in section IV.

IV. Experimental Results

(1) Expression of Results

It is possible to express the difference between a standard and an unknown in two ways. At times, the actual temperature difference between the reference temperatures for the two samples is reported. In other plants, this difference in converted to the actual density difference by means of the factor for the net change of density with temperature that is discussed under section II (3). As long as the same individual lump is used for the standard, density variations may be expressed simply as differences from this standard lump. When more than one standard lump is used, however, it is necessary to calibrate these standards before intercomparisons of the density differences found with them can be made.

This may be done in terms of a single, master standard or in terms of their absolute densities. If comparisons are to be made between values found in various plants or laboratories, the absolute densities are especially important. These absolute densities give permanent records independent of the possible loss of the special standard lumps; they allow a universal expression of the density values independent of the particular method and laboratory. It is believed advisable to have the standard lumps calibrated in every case. The simple temperature differences, however, are useful as daily values for production control purposes and are recommended for use on control charts. Then any particular value can be converted to the corresponding absolute density if such is desired.

(2) Method of Calculation

In case simple temperature differences are to be used to express the densities, obviously, no calculations are needed. If, instead, control charts are to be plotted in terms of the differences expressed in density units, the factor for the change of density with temperature must be used. The use of this factor is very simple; to get the density differences, the temperature differences are multiplied by the factor as shown in equation (1).

$$\Delta D = F(T_x - T_s) \tag{1}$$

ΔD = density difference (gm./cc.).
F = temp.-density factor; with the present liquids, this is -0.00171 gm./cc./°C. for flint glasses and -0.00174 for borosilicate glasses.
T_x = reference temp. for unknown (°C.).
T_s = reference temp. for standard (°C.).

If ΔD is positive, the unknown lump is denser than the standard, whereas, if the lump is less dense, ΔD is negative. The algebraic addition of ΔD to the absolute density of the standard, D_s, will yield the absolute density of the unknown, D_x, as shown in equation (2).

$$D_x = D_s + F(T_x - T_s) \tag{2}$$

This equation gives the absolute density of the unknown glass at the same temperature as that at which the standard glass was calibrated.* Usually, 20°C. is used as this standard temperature.

(3) Sample Calculations

Typical data taken on four successive days on a single shop are given in Table I together with the results of calculations made by equation (2).

TABLE I

TYPICAL DATA AND DENSITY VALUES

Sample No.	Reference temp. (°C.) Standard T_s*	Reference temp. (°C.) Unknown T_x	Density difference (°C.) $(T_x - T_s)$	Density difference (gm./cc.) $F(T_x - T_s)$	Absolute density at 20°C. (gm./cc.)
1	29.89	28.02	−1.87	0.0032	2.5079
2	29.82	29.61	−0.21	0.0004	2.5051
3	30.07	30.40	0.33	−0.0006	2.5041
4	29.94	31.22	1.28	−0.0022	2.5025

* Single standard lump run in same tube on 4 days; density of standard at 20°C. = 2.5047 gm./cc.

The details of the use of equation (2) are illustrated below for the data of sample 1 of Table I; careful attention must be paid to algebraic signs in these calculations.

$$\begin{aligned} D_x &= D_s + F(T_x - T_s) \qquad (2)\\ &= 2.5047 + (-0.00171)(28.02 - 29.89)\\ &= 2.5047 + (-0.00171)(-1.87)\\ &= 2.5047 + 0.0032\\ D_x &= 2.5079 \text{ gm./cc. at } 20\,^\circ\text{C.} \end{aligned}$$

It is obvious that the denser of two lumps will settle at a lower temperature than the less dense lump; this fact can be used as a convenient check on the calculations. If the unknown lump settles at a lower temperature than the standard, the density difference is to be added to the density of the standard, and, conversely, if the unknown settles at a higher temperature than the standard, the density difference is to be subtracted. With experience, most operators come to recognize these relationships and so do not need to use equation (2) as such. A table of temperature differences multiplied by the factor F is very useful in determining the density differences. The calculations are thus very simple and much more rapid than those of the Archimedes method.

V. Precision of Method

The precision of the present method appears to be equal to or better than those of the other techniques useful for the determination of lump densities. This precision has been determined by successive tests made on many samples in this laboratory and in a plant laboratory. Careful work yields a standard deviation of

* For complete discussion of this type of calculation, see Knight, footnote 1 (*i*).

about ±0.0001 gm. per cc. for successive determinations on individual lumps. Statistically, this indicates that 67% of the measurements will be in error by not more than ±0.0001 gm. per cc., 94% by not more than ±0.0002 gm. per cc., and 99.7% by not more than ±0.0003 gm. per cc.

Composition heterogeneity can introduce considerable density differences between various lumps taken from a single piece of ware; these differences will be several times the standard deviation of ±0.0001 gm. per cc. The spread in density between various lumps from a piece of ware indicates the degree of homogeneity of the glass in question.*

VI. Advantages of Method

The present method is precise, simple, and easily operated. It is more rapid than the other variations of the sink-float technique and much more so than the Archimedes method or any pycnometer methods. In a single run, twenty to thirty lumps can be tested completely within 30 to 45 minutes from the time the ware is taken from the lehr. Thus, even in a large plant, regular testing can be handled quickly and efficiently. The method is especially valuable in the case of trouble-shooting work involving cordy glass, since complete surveys can be made often and quickly.

Because of its simplicity, fewer chance errors or mistakes are likely to enter into the method than in the more complicated techniques. This is important especially when inexperienced operators are making the determinations. The method is probably more precise than the other possible tests; measurements show a standard deviation of about ±0.0001 gm. per cc. It undoubtedly excels the Archimedes method when both are carried out by relatively unskilled technicians in a plant laboratory.

From the density results obtained from a single run on several lumps from a piece of ware, not only is the representative density available, but there is also some measure of the homogeneity of the ware. This is a distinct advantage over the Archimedes or pycnometer methods. The density-spread results, naturally, do not approach the detailed, density distributions obtained by the stroboscopic-centrifuge technique which uses 100- to 200-mesh powders. Where the time-consuming procedure of the centrifuge method is not warranted, however, a useful indication of homogeneity is given very quickly by the settling method.

VII. Summary

This method offers a rapid, precise, and convenient technique for measurements of glass densities in glass plants; both the representative glass density and a measure of glass heterogeneity are obtained on each test. In a single run, densities of as many as 30 lumps (six tubes with five unknown lumps in each) can be completely determined within 30 to 45 minutes from the time the ware is taken from the lehr.

As well as being much more rapid than the other available methods, the present method is, in general, more precise. The standard deviation of the measurements obtained by this technique is about ±0.0001 gm. per cc. The simplicity of the procedure and the apparatus makes the settling method especially appropriate when relatively untrained operators are to be used.

Certain precautions as to sampling, both in selection of the ware and in cutting the test lumps from this ware, must be observed if the greatest possible value is to be obtained from density measurements; this is true no matter what method is used. No reannealing of the samples is necessary when the lumps are taken as described herein.

The settling method is recommended for glass-plant control work. It greatly facilitates the use of statistical control charts based on daily density measurements and is especially useful in cases of unusual glass heterogeneity problems.

Acknowledgment

The author wishes to acknowledge the kind cooperation of the members of the Technical Sub-Committee of the Glass Container Association of America and, in particular, the Owens-Illinois Glass Company, the Hazel-Atlas Glass Company, and the Armstrong Cork Company, who made available their laboratory experience in using sink-float baths.

PRESTON LABORATORIES
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* The total spread obviously includes that due to annealing effects; a spread of about 0.0004 gm. per cc. is possible in commercially good annealing as previously discussed. The density spreads due to composition differences overshadow the annealing effects in most cases. Further quantitative work on the effect of annealing is in progress.

GLASS COMPOSITION AND DENSITY CHANGES*

By Robert M. Elliott

Abstract

A set of factors is derived for calculating the glass density changes caused by moderate changes in composition. These are similar to those of Ghering and Knight but indicate that portion of the total density change due to each oxide. They also give directly the approximate density change caused by dilution.

I. Introduction

The calculation of the changes in glass density caused by moderate changes in composition may be conveniently performed by the use of density difference factors. Such a set of factors has been proposed by Ghering and Knight[1]; their Y_m factors are given by equation (1) and the density change by equation (2).

$$Y_m = \frac{-0.01\rho^2}{Z_m} \tag{1}$$

$$\Delta\rho = Y_1\,\Delta X_1 + Y_2\,\Delta X_2 + Y_3\,\Delta X_3 + \ldots \tag{2}$$

ρ = density (gm./cc.).
Z_m = Huggins density factor (see footnote 2).
X_m = weight % of component oxide.

The absolute values of these Y_m factors of Ghering and Knight are, however, quite arbitrary since an arbitrary quantity (K) may be added to each factor without changing the calculated value of $\Delta\rho$. If X_m represents the weight percentage of oxide M,

$$\Delta\rho = (Y_1 + K)\Delta X_1 + (Y_2 + K)\Delta X_2 + (Y_3 + K)\Delta X_3 + \ldots$$

$$= Y_1\,\Delta X_1 + Y_2\,\Delta X_2 + Y_3\,\Delta X_3 + \ldots + K(\Delta X_1 + \Delta X_2 + \Delta X_3 + \ldots)$$

But $\Delta X_1 + \Delta X_2 + \Delta X_3 + \ldots = 0$ for any composition change.

Hence $\Delta\rho = Y_1\,\Delta X_1 + Y_2\,\Delta X_2 + Y_3\,\Delta X_3 + \ldots$

This arbitrary nature of the Y_m factors may be quite misleading. The factors do not indicate directly the density change ascribable to each oxide and thus do not indicate the relative importance of each oxide in affecting density changes. All Y_m factors, moreover, are negative, indicating a decrease in density for an increasing amount of any oxide; this is not in accord with known facts.

II. Derivation of New Factors

A more rational set of factors may be derived. Consider a sample of glass of density ρ and suppose that component having a Huggins factor, Z_m, is added in a fractional amount, f. The new glass will then have a density ρ', and the original glass will be present in the fractional amount $\frac{1}{1+f}$, while the added component will be present in the fractional amount $\frac{f}{1+f}$

By the additive theory of specific volumes, equation (3) results.

$$\frac{1}{\rho'} = \frac{1}{(1+f)\rho} + \frac{f}{(1+f)Z_m}$$

But $\Delta\rho = \rho' - \rho$

$$\text{Then } \Delta\rho = \rho f\left(1 - \frac{\rho'}{Z_m}\right) \tag{3}$$

Equation (4) shows the density change for a moderate change in composition and equation (5) for changes of several components.

$$\rho' \cong \rho, \text{ or } \Delta\rho = \rho f\left(1 - \frac{\rho}{Z_m}\right) \tag{4}$$

$$\Delta\rho = Y'_1\,\Delta X_1 + Y'_2\,\Delta X_2 + Y'_3\,\Delta X_3 + \ldots. \tag{5}$$

$$Y'_m = 0.01\rho\left(1 - \frac{\rho}{Z_m}\right) \tag{6}$$

It is obvious that the factors given by equation (6) are the same as those of Ghering and Knight except that 0.01ρ has been added to each. They have, however, the following desirable properties: (1) They are applicable to a general composition change where the weight percentage of several oxides is changed (provided the changes are small); this is the only case where the Y_m factors are applicable; (2) they will give directly the density change due to simple dilution, for example, as an increase in batch weight of one component; the Y_m factors will not do this; (3) they are small; and (4) their signs and magnitudes indicate directly the density changes ascribable to each oxide in a composi-

Table I

Factors for Calculation of Density Differences

Oxide	Density change (gm./cc./%) Y_m*	Y'_m
SiO_2	−0.0273	−0.0024
Al_2O_3	−0.0232	+0.0018
CaO	−0.0143	+0.0106
MgO	−0.0199	+0.0050
BaO	−0.0075	+0.0173
Na_2O	−0.0200	+0.0050
K_2O	−0.0222	+0.0028
B_2O_3	−0.0281	+0.0036
ZnO	−0.0105	+0.0145
PbO	−0.0056	+0.0192

* See Ghering and Knight, footnote 1.

* Received March 15, 1945; revised copy received June 14, 1945.

[1] L. G. Ghering and M. A. Knight, "Properties and Diagnosis of Cords in Pressed and Blown Glassware," *Jour. Amer. Ceram. Soc.*, **27** [9] 260–66 (1944).

[2] M. L. Huggins and K.-H. Sun, "Calculation of Density and Optical Constants of Glass from Composition in Weight Percentage," *ibid.*, **26** [1] 4–11 (1943).

TABLE II

SUBSTITUTION OF VARIOUS OXIDES IN GLASS

By Y_m factors*	By Y'_m factors
(*a*) 1% SiO_2 replaced by 1% Al_2O_3	
SiO_2: $-1.0 \times -0.0273 = +0.0273$	SiO_2: $-1.0 \times -0.0024 = +0.0024$
Al_2O_3: $+1.0 \times -0.0232 = -0.0232$	Al_2O_3: $+1.0 \times +0.0018 = +0.0018$
Density change = +0.0041 gm./cc.	Density change = +0.0042 gm./cc.
(*b*) 1% CaO replaced by 1% Al_2O_3	
CaO: $-1.0 \times -0.0143 = +0.0143$	CaO: $-1.0 \times +0.0106 = -0.0106$
Al_2O_3: $+1.0 \times -0.0232 = -0.0232$	Al_2O_3: $+1.0 \times +0.0018 = +0.0018$
Density change = −0.0089 gm./cc.	Density change = −0.0088 gm./cc.
(*c*) 1% SiO_2 replaced by 1% Na_2O	
SiO_2: $-1.0 \times -0.0273 = +0.0273$	SiO_2: $-1.0 \times -0.0024 = +0.0024$
Na_2O: $+1.0 \times -0.0200 = -0.0200$	Na_2O: $+1.0 \times +0.0050 = +0.0050$
Density change = +0.0073 gm./cc.	Density change = +0.0074 gm./cc.
(*d*) 1% CaO replaced by 1% Na_2O	
CaO: $-1.0 \times -0.0143 = +0.0143$	CaO: $-1.0 \times +0.0106 = -0.0106$
Na_2O: $+1.0 \times -0.0200 = -0.0200$	Na_2O: $+1.0 \times +0.0050 = +0.0050$
Density change = −0.0057 gm./cc.	Density change = −0.0056 gm./cc.

* See Ghering and Knight, footnote 1.

tion change involving any number of oxides; all of the Y_m factors are negative and their magnitudes do not indicate the relative importance of each oxide in affecting the density.

The new factors are shown in Table I along with those of Ghering and Knight. They are calculated for a bottle glass of density 2.49 gm. per cc. having a silica content of 69 to 75%. The same factors, however, will apply to a similar glass in the density range of 2.45 to 2.53 with a maximum error of ±0.0005 gm. per cc. if the change in composition does not exceed 1%. A similar set of factors may be derived for any other glass.

In the case of simple dilution, such as may occur after a batch change, the Y'_m factors will give directly the change in density caused by the increase (or decrease) of one oxide. This avoids the necessity of computing the old and new glass compositions and then applying the density factors in accordance with the change in each oxide. The proof of this relationship is as follows:

Let X_1 be the weight percentage of oxide 1 in the glass; let X_m be the weight percentage of any other oxide; and let the glass be diluted by adding oxide 1 in fractional amount f; then, considering a unit weight of glass before dilution, equations (7) and (8) result.

Since the Y'_m factors are restricted to small changes, equation (9) results.

Equations (10) and (11) may be written for any other oxide.

Equation (12) is obtained by using the Y'_m factors for each oxide.

$$X'_1 = 100\,\frac{0.01X_1 + f}{1 + f} = \frac{X_1 + 100f}{1 + f} \qquad (7)$$

$$\Delta X_1 = X'_1 - X_1 = \frac{f}{1 + f}(100 - X_1) \qquad (8)$$

$$\Delta X_1 \cong f(100 - X_1) \qquad (9)$$

$$X'_m = 100\,\frac{0.01X_m}{1 + f} = \frac{X_m}{1 + f} \qquad (10)$$

III. Examples

As an example of the use of the foregoing factors, Table II shows the density changes caused by substitution of various oxides and calculated by using both the Y'_m and Y_m factors. The minor discrepancies which exist between the two sets of results are due to slight differences in calculation of the factors.

For an example of the application of the Y'_m factors to a case of simple dilution, a glass composition is considered in Table III.

TABLE III

APPLICATION OF DENSITY-DIFFERENCE FACTORS TO SIMPLE DILUTION OF GLASS COMPOSITION

Batch			Calculated glass composition		
Material	Composition (%)	Wt. (lb.)	Oxide	Wt. (lb.)	X_m (%)
Sand		1000	SiO_2	1065	71.87
Soda ash	58 Na_2O	400	Na_2O	232	15.65
Feldspar	65 SiO_2	100			
(Microline)	18 Al_2O_3		Al_2O_3	18	1.21
	17 K_2O		K_2O	17	1.15
Burnt lime		150	CaO	150	10.12
		1650		1482	100.00

If the sand weight is now increased, for example, by 1% of the glass weight, the density change according to the Y'_m factor is shown by equation (16). This change may also be calculated, more laboriously, by using the Y'_m or Y_m factors for each oxide as shown in Table IV.

$$\Delta\rho = Y'_1\,\Delta X_1 = (-0.0024)\,(1) = -0.0024 \text{ gm./cc.} \qquad (16)$$

Density change by various factors

Y'_m, −0.0027 gm./cc.
Y_m, −0.0025 gm./cc.
Y'_m, for silica only, −0.0024 gm./cc.

$$\Delta X_m = X'_m - X_m = -X_m \frac{f}{1+f}$$

$$\text{or } \Delta X_m \cong -X_m f \qquad (11)$$

$$\Delta\rho = \Sigma Y'_m \Delta X_m = Y'_1 \Delta X_1 + Y'_2 \Delta X_2 + \ldots.$$

$$= Y'_1 f(100 - X_1) - Y'_2 f X_2 - Y'_3 f X_3 - \ldots.$$

$$= 100 f Y'_1 - f(Y'_1 X_1 + Y'_2 X_2 + Y'_3 X_3 + \ldots.) \qquad (12)$$

Since $Y'_m = 0.01\rho\left(1 - \frac{\rho}{Z_m}\right)$, the equation for $\Delta\rho$ is shown in (13), (14), and (15).

$$\Delta\rho = 100 f Y'_1 - 0.01 f\rho\left[\left(1 - \frac{\rho}{Z_1}\right)X_1 + \left(1 - \frac{\rho}{Z_2}\right)X_2 + \ldots.\right] \qquad (13)$$

$$= 100 f Y'_1 - 0.01 f\rho\left[X_1 + X_2 + X_3 + \ldots. - \rho\left(\frac{X_1}{Z_1} + \frac{X_2}{Z_2} + \ldots.\right)\right]$$

But $X_m = 100 f_m$, so,

$$\Delta\rho = 100 f Y'_1 - 0.01 f\rho\left[100 - 100\rho\left(\frac{f_1}{Z_1} + \frac{f_2}{Z_2} + \ldots.\right)\right] \qquad (14)$$

But $\frac{f_1}{Z_1} + \frac{f_2}{Z_2} + \ldots. = \frac{1}{\rho}$

$$\text{Hence } \Delta\rho = 100 f Y'_1 = Y'_1 \Delta X_1 \qquad (15)$$

This is just the result obtainable by considering the change in oxide 1 alone.

TABLE IV

CALCULATION OF DENSITY CHANGE

Silica Increased by 1% of Glass Weight

Calculated glass composition				Calculated density change			
				By Y'_m factors		By Y_m factors	
Oxide	Wt. (lb.)	X_m (%)	ΔX_m (%)	Y'_m	$Y'_m \Delta X_m$	Y_m	$Y_m \Delta X_m$
SiO_2	1079.8	72.14	+0.27	−0.0024	−0.00064	−0.0273	−0.00736
Na_2O	232	15.50	−0.15	+0.0050	−0.00075	−0.0200	+0.00300
Al_2O_3	18	1.20	−0.01	+0.0018	−0.00018	−0.0232	+0.00023
K_2O	17	1.14	−0.01	+0.0028	−0.00003	−0.0222	+0.00022
CaO	150	10.02	−0.10	+0.0106	−0.00106	−0.0143	+0.00143
	1496.8	100.00	0.00		−0.00266		−0.00248

IV. Summary

The Y'_m factors are shown to have the same applicability as the Y_m factors of Ghering and Knight, plus the added advantage of giving directly the density changes caused by dilution, as in a batch change. The main argument, however, in favor of the Y'_m factors is that by their sign and magnitude they indicate the density changes due to each oxide even in the case of a complicated composition change. To the casual observer, the Y_m factors of Ghering and Knight will be misleading whereas the Y'_m factors clearly show, for example, that calcia is about five times as influential in causing density changes as is silica or alumina.

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EFFECT OF CHEMICAL COMPOSITION ON RELATIONSHIP BETWEEN REFRACTIVE INDEX AND ABBE VALUE FOR BINARY SYSTEMS*

By Kuan-Han Sun and Maurice L. Huggins

Abstract

A procedure is outlined for deriving the relationship between n_D and ν for binary glass systems, using constants previously published by Huggins and Sun.[1] As an example, the Na_2O–SiO_2 system is discussed and the results are plotted in two ways. An equation is deduced for the slope of the n_D versus ν curve at any composition, and initial values of this slope, at the SiO_2 end, are tabulated for various M_mO_n–SiO_2 systems.

I. Introduction

The most familiar chart in the field of optical glass is the plot of refractive index (n_D) against Abbe value (ν), the latter being defined in equation (1).

$$\nu \equiv \frac{n_D - 1}{n_F - n_C} \equiv \frac{\mu_D}{n_F - n_C} \tag{1}$$

n_F, and n_C = refractive indices of spectrum lines F and C.
$\mu_D \equiv n_D - 1$.

In these graphs, as usually prepared, empirical data are plotted and the dependence on chemical composition is indicated only roughly, if at all. It is of interest to show this dependence on composition more clearly and comprehensively. The purpose of this paper is to show how this can be done for simple cases, using relationships of proved validity. For the present, only binary systems, such as can be represented by the general formula M_mO_n–SiO_2 are considered.

Let subscripts 1 and 2 designate compositions or properties related to SiO_2 and M_mO_n, respectively. Huggins and Sun[1] have shown that n_D and ν can be calculated from compositions and constants evaluated by them by means of equations which reduce (for the case described here) to equations (2) and (3).

$$\mu_D \equiv n_D - 1 = \frac{r_2 + f_1(r_1 - r_2)}{v_2 + f_1(v_1 - v_2)} \tag{2}$$

$$\nu = \frac{r_2 + f_1(r_1 - r_2)}{r_{2,FC} + f_1(r_{1,FC} - r_{2,FC})} \tag{3}$$

Here f = weight fraction.
r = specific refraction constant for D line.
r_{FC} = difference between specific refraction constants for the F and C lines.
v = specific volume constant, having different values for different ranges of N_{Si}.

$$N_{Si} = N_1 = \frac{f_1}{60.06[s_2 + f_1(s_1 - s_2)]} \tag{4}$$

s = ratio of number of oxygens represented in formula of given component to formula weight of that component.

Equation (5) is obtained by combining equations (2) and (3) and eliminating f_1.

$$\mu_D = \frac{(r_{2,FC}r_1 - r_{1,FC}r_2)\nu}{(r_{2,FC}v_1 - r_{1,FC}v_2)\nu + (r_1v_2 - r_2v_1)} = \frac{\nu}{a\nu + b} \tag{5}$$

$$\text{Here } a = \frac{r_{2,FC}v_1 - r_{1,FC}v_2}{r_{2,FC}r_1 - r_{1,FC}r_2}$$

$$b = \frac{r_1v_2 - r_2v_1}{r_{2,FC}r_1 - r_{1,FC}r_2}$$

This is the relationship sought; here, r_1, r_2, $r_{1,FC}$ and $r_{2,FC}$ are constants which in most cases are independent of composition, while v_1 and v_2 are constant within a given composition range but with different values in different ranges. The v_1 and v_2 values applicable to a glass are determined by the values of N_{Si}. To cover adequately the glasses for which experimental data are available, four sets of v_1 and v_2 values are required. These and the r values for different components are tabulated in the Huggins and Sun paper.[1] Corresponding to the four pairs of v_1 and v_2 values, there are four sets of equations relating μ_D and ν.

Equation (5) can easily be converted into equation (6). This indicates that if $1/\mu_D$ is plotted against

$$\frac{1}{\mu_D} = a + b\left(\frac{1}{\nu}\right) \tag{6}$$

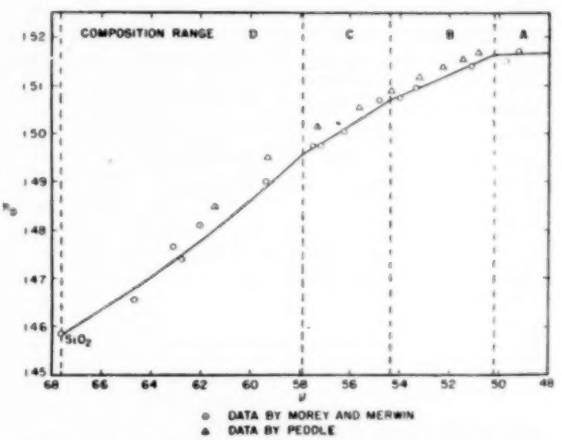

Fig. 1.—Relationship between n_D and ν for Na_2O–SiO_2.

* Received June 20, 1945.
Communication No. 1039 from the Kodak Research Laboratories.

[1] M. L. Huggins and K.-H. Sun, "Calculation of Density and Optical Constants of Glass from Its Composition in Weight Percentage," *Jour. Amer. Ceram. Soc.*, **26** [1] 4–11 (1943).

TABLE I

CONSTANTS FOR THE Na_2O–SiO_2 SYSTEM

N_{Si}	$f_1 = f_{Si}$	ν	$\frac{1}{\nu}$	Region	a	b
0.500	1.0000	67.6	0.01479			
				D	3.1671	−66.577
.435	0.7643	57.9	.01727			
				C	2.7195	−40.663
.400	0.6596	54.4	.01838			
				B	2.4021	−23.385
.345	0.5188	50.2	.01992			
				A	1.9904	− 2.655
.27	0.3625	46.2	.02165			

$1/\nu$, a straight line should result for each composition range.

II. Example

As an example, the constants a and b for the system Na_2O–SiO_2 have been calculated and are listed in Table I.

Four equations, each of the form of equation (5), are obtained. Plotting each of these in its appropriate region gives the composite curve shown in Fig. 1. For comparison, the experimental data by Peddle[2] and by Morey and Merwin[3] are also plotted on the same diagram. Peddle's glasses were melted in clay pots and may contain some impurities, so that the actual compositions may differ from the batch compositions, assumed to be correct. This may be the reason that his experimental points lie above those representing the Morey and Merwin glasses. The constants used in obtaining the curves were deduced from the more accurate data by Morey and Merwin; hence their experimental points agree better with the composite curve of Fig. 1 than do the Peddle points.

Similarly, four equations of the form of equation (6) have been obtained and plotted in Fig. 2.

III. Initial Slopes

Equation (7) is obtained by differentiating equation (5).

$$\frac{d\mu_D}{d\nu} = \frac{dn_D}{d\nu} = \frac{(r_{2,FC}r_1 - r_{1,FC}r_2)(r_1v_2 - r_2v_1)}{[(r_1v_2 - r_2v_1) + (r_{2FC}v_1 - r_{1FC}v_2)\nu]^2} = -\frac{b}{(a\nu + b)^2} \quad (7)$$

This equation gives the slope of the curve for any given composition in the n_D versus ν plot of a binary system.

TABLE II

INITIAL RATE OF CHANGE OF REFRACTIVE INDEX WITH ABBE VALUE FOR ADDITION OF A SECOND COMPONENT TO PURE SiO_2

M_mO_n	$10^3\left(\frac{dn_D}{d\nu}\right)_{f_{Si}=1}$	M_mO_n	$10^3\left(\frac{dn_D}{d\nu}\right)_{f_{Si}=1}$
Li_2O	− 7.6	BaO	−26.0
Na_2O	− 3.1	PbO	− 9.1
K_2O	− 3.9	$B_2O_3(B^{IV})$	−38.3
Rb_2O	− 0.4	Al_2O_3	−11.3
Tl_2O	− 1.0	Bi_2O_3	− 2.1
MgO	− 6.5	TiO_2	− 1.9
CaO	−10.0	ZrO_2	− 3.9
ZnO	− 4.5	Ta_2O_5	− 2.9
SrO	−11.8		

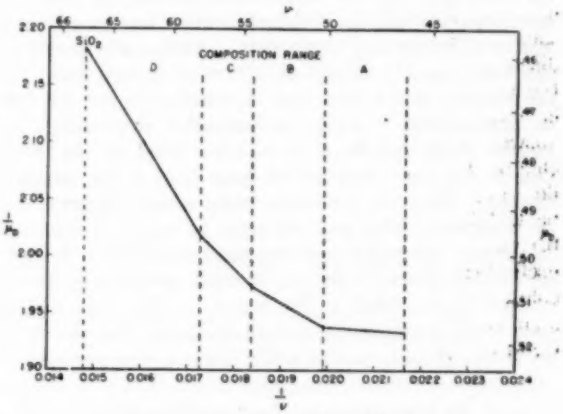

FIG. 2.—Relationship between $\frac{1}{\mu_D}$ and $\frac{1}{\nu}$ for Na_2O–SiO_2.

The initial slopes for the addition of small amounts of other constituents to pure silica are calculated by substituting the appropriate constants. The values obtained are listed in Table II. It should be noted that the accuracy of these values is limited by the accuracy of the original literature data from which the Huggins and Sun constants were derived.

Relationships between n_D and ν for polycomponent systems can be derived in a manner analogous to that just described. The equations obtained, as would be expected, are considerably more complex.

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[2] C. J. Peddle, "Development of Various Types of Glass, I-V," *Jour. Soc. Glass Tech.*, **4**, 3–107 (1920); extended abstract in *Jour. Amer. Ceram. Soc.* (*Ceram. Abs.*), **3** [8] 681–83 (1920).

[3] G. W. Morey, Properties of Glass, pp. 376, 383–86. Amer. Chem. Soc. Monograph Series, No. 77. Reinhold Publishing Corp., New York, 1938. 561 pp.; *Ceram. Abs.*, **18** [2] 48 (1939).

TRACING FLOW IN GLASS TANK FURNACES*

By F. L. Bishop, Jr.

Abstract

By adding a small amount of a rare earth to a definite portion of batch, the velocity, direction, and amount of surface flow can be determined. The flow measurements are calculated from the resultant slight fluorescence of samples taken at intervals or by the change in transmission for certain wave lengths of ultraviolet light. Sample results are shown and discussed.

I. Introduction

The enigma of what happens in a glass tank between the melting of the raw batch materials and the time the machines produce the finished product has long been a source of interesting arguments. Among the questions discussed are (1) the speed of flow of molten glass, (2) the amount that moves, and (3) whether or not the flow is streamlined. Many unsuccessful approaches to answer these questions have been tried in the past. One of the most common of these tests is the use of a floating, relatively insoluble body whose progress can be watched. This method may be open to question because it measures only surface conditions. A more useful experiment is the use of small amounts of highly colored glass added to the batch. This glass can be seen when it appears in certain machines, but the quality of the glass is spoiled while the test is in progress.

II. Methods of Testing Glass Flow

The process described in this paper is similar to the second test except that the material added causes no visible change in the glass produced. It may be detected by its fluorescence or by a change in ultraviolet absorption. Some of the rare earth elements, particularly cerium, give this effect.

In actual use, an amount of batch and cullet sufficient to charge for about one hour is mixed with about 0.3% of cerium hydrate. The time of the start and finish of the charging of this batch are taken. Samples of the glass are then taken at regular intervals from various points in the melting and refining sections of the tank. These samples may be merely short rods drawn out on an iron tip; these are examined under filtered ultraviolet light, and the time (frequency) of arrival of the cerium-containing glass is noted. These measurements are qualitative, but they can be made quantitative by measuring with a fluorimeter.

Figure 1 shows transmission curves for a clear glass and for glass containing approximately 0.01% oxide weight of cerium. The curves appear to be very close together, but at the wave length of greatest difference there is about 10% difference; this wave length is approximately 325 mμ. A glass batch containing one tenth this amount of cerium shows a characteristic fluorescence under the light from a quartz mercury arc filtered through a glass such as Corning No. 5874. The visible transmission is unchanged.

The second test was performed by taking measurements on the completed product. Because this product is sheet glass, actual measurements of the relative amount of cerium present at any time and on any machine can be made by measurements of the absorption of ultraviolet light.

III. Test Procedure

In order to make actual measurements, samples were taken from the machines at different times before any cerium-containing batch was added. The transmission for light in a narrow region around 325 mμ was de-

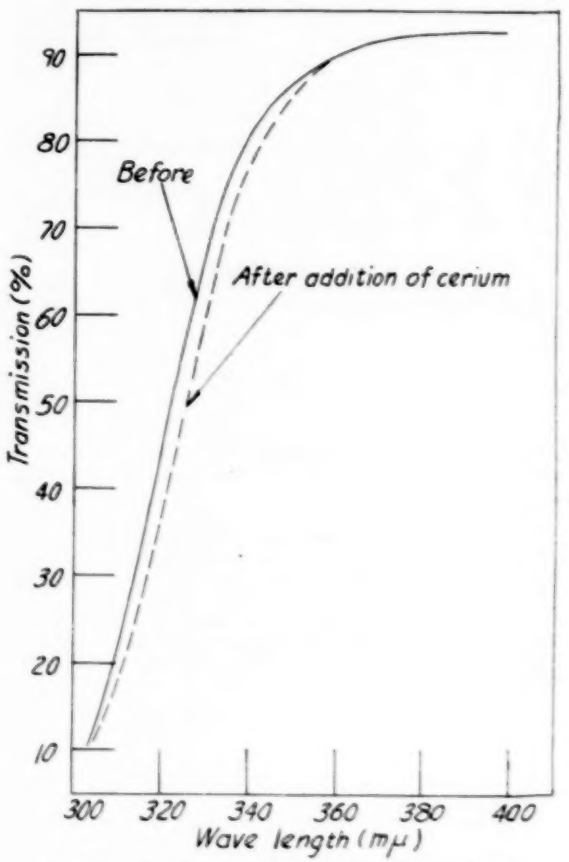

Fig. 1.—Results on addition of cerium to glass.

* Forty-Seventh Annual Program, The American Ceramic Society (Glass Division, No. 12). Received May 12, 1945.

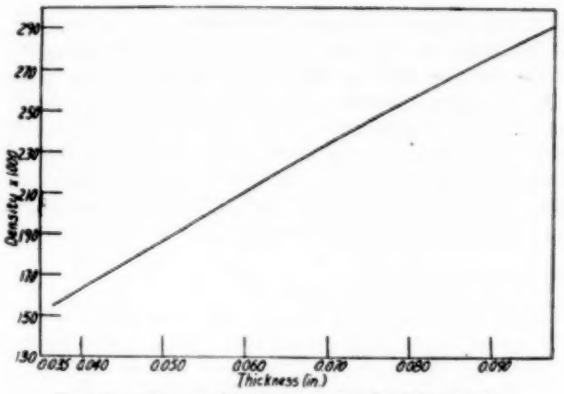

FIG. 2.—Curve obtained as standard for tests.

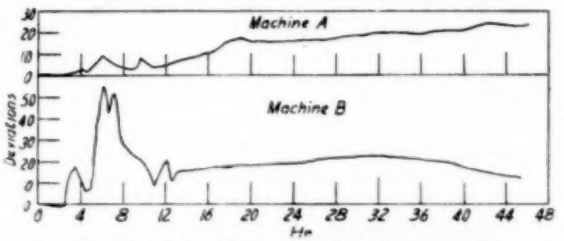

FIG. 3.—Deviation-time curves for single machines.

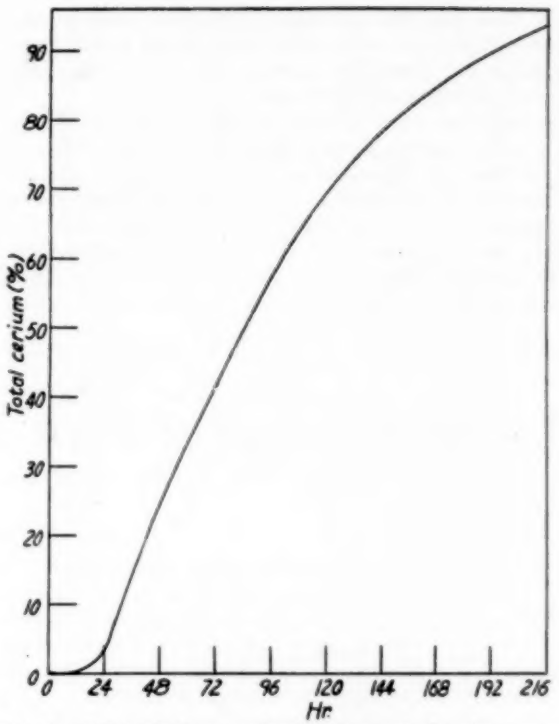

FIG. 4.—Integrated curve showing amount of cerium-containing batch already through machines.

termined for various thicknesses of glass. Figure 2 shows the curve obtained for these optical densities plotted against thickness, and this curve was used as a standard. When the effect of the added cerium was felt at the machines, densities higher than this curve were obtained. The difference was calculated between the density actually measured on a sample and the value from the standard curve for the actual thickness of the sample. If the Beer-Lambert law is followed, these values would be proportional to the percentage of cerium in the glass, or they should at least give a relative measure. Figure 3 shows the curves obtained when all of the results from one machine were plotted against time. Actual chemical analyses showed that a deviation of 14 units from the standard curve at 0.100 in. thickness meant approximately 0.002% cerium oxide.

In order to check on the probable error of these determinations, one thousand samples were taken during a period of two days before any cerium was added; these samples were calculated just as if they contained cerium. A value for the deviation of zero for each sample should have been obtained. Actual measurements, however, showed a probable error of a single measurement to be ±1.2 points, which means approximately ±0.0002% of cerium.

Several kinds of information were obtained from the deviation-time curves for single machines such as those shown on Fig. 3. For example, the time of arrival of the cerium-containing glass at each machine, that is, the curve for machine A of Fig. 3, shows significant deviations at 4 hours and for machine B, at 2½ hours, which gives a measure of average surface flow rates. The time for each machine on a tank was found, and it was possible to know which machines to watch for the first indications of any change in composition of the batch. Great differences were found between the various machines on a single tank, both in time of arrival and in the shape of the curve. Some machines were shown to be receiving large quantities of recently melted batch, as in machine B, whereas others like machine A showed much slower effects. An interesting feature of nearly all the curves was the plurality of peaks, indicating that the flow of glass was occurring over more than one path.

Because a correlation between deviation and chemical analysis was obtained, each point on these curves represents a definite amount of the original cerium. For example, the highest point on the curve for machine B represents a half-hour period during which the deviation was 55 units, which is roughly equivalent to 0.008% of cerium oxide. Since the number of pounds of glass actually made on machine B during this period is known, it is possible to estimate the approximate number of pounds of the original cerium hydrate. By translating each point on all machines for one hour, the number of pounds of cerium hydrate which appear in the glass during that hour may be calculated. This process is repeated as long as deviations occur and until all of the original cerium addition is accounted for. Figure 4 is an integrated curve showing the percentage of cerium already processed through the machines. The points on this curve show that 84 hours after the introduction of the cerium-containing batch 50% of the batch has become glass; in other words, of the glass being drawn at any time, 50% has been in

the tank less than 84 hours. Another point in this curve shows that of the glass being drawn at any time, a small but significant portion, about 1%, has been in the tank less than 12 hours.

This same type of integrated curve could be drawn for each machine because all of the machines draw at approximately the same rate and each would thus account for its proportion of the original cerium. For example, Fig. 3 would show that on machine A, of the glass drawn at any time, less than 0.1% had been in the tank less than 8 hours; but on machine B, it shows that nearly 1% had been in the tank less than 8 hours.

IV. Conclusions

All of the figures given here are necessarily approximate because they are based on several assumptions. They do give, however, a relatively clear picture of the progress of the glass batch to the finished product. By combining the observations made on samples dipped from the tank at various times and the measurements made on finished products, the rate of flow as well as the total amount of flow can be determined.

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VISCOSITY STUDIES OF SYSTEM CaO–MgO–Al_2O_3–SiO_2: I, 40% SiO_2*

BY J. S. MACHIN AND D. L. HANNA

ABSTRACT

The measurement of glass viscosities at elevated temperatures with an oscillating cylinder-type viscometer is described. Viscosity data are presented covering those compositions in the CaO–MgO–Al_2O_3–SiO_2 system which contain 40% SiO_2 and which are liquid at 1500°C. The pattern of the system of isokoms presented indicates that viscosity is closely related to the ratio of basic to acidic components. Theoretical aspects of the variation of viscosity with composition in silicate-aluminate systems are discussed in terms of silica-alumina polymers.

I. Introduction

The interest in high-temperature viscosity data is attested by the number of workers who, despite the experimental difficulties which beset such investigations, have made measurements of viscosities of slags and glasses. The severity of the conditions, particularly the high temperatures, and the corrosive character of many of the most important types of slags have resulted in many concessions in apparatus design, and, as a result, the reliability of the data may, in some instances, be questioned on theoretical as well as on practical grounds. For instance, although it is well known that the viscosity function is extremely sensitive to temperature changes, the high-frequency induction furnace has been used for slag viscosity studies. This type of furnace is difficult to control within narrow limits of temperature. Temperatures of 1600°C. and even much higher are easily obtained with it. These high temperatures, although desirable because many metallurgical operations involving slags employ them, rule out the use of platinum for viscometer parts. They also drive the experimenter to the use of optical or radiation pyrometers for temperature measurement and control. The records of optical pyrometers are affected by layers of heated gases in the space intervening between the surface whose temperature is being measured and the sensitive element if the temperatures of gas and surface are different. It seems probable that the radiation type would also record a temperature intermediate between that of the gas and of the surface.[1] It is doubtful whether the use of emissivity and other corrections can compensate for all of the factors affecting the readings of such pyrometers sufficiently well to meet the problem posed by the sensitivity of viscosity to temperature change.

The use of graphite as a material for viscometer parts has been questioned because it is not wet by molten slags and glasses. McCaffery[2] used a Margules-type viscometer modified by employment of a square spindle. He states that this spindle removed most of the objections inherent in the cylindrical spindle. He did not, however, present any theoretical or practical justification for the use of a square spindle; at least, he made no mention of calibration against any liquid other than castor oil. It would appear to be desirable to calibrate against liquids with a considerable range of viscosities when using such a spindle.

* Received August 14, 1945.

These viscosity studies grew out of mineral wool studies made in this laboratory and reported in two papers as follows: (*a*) J. E. Lamar, H. B. Willman, C. F. Fryling, and W. H. Voskuil, "Rock Wool from Illinois Mineral Resources," *Illinois Geol. Survey Bull.*, No. 61, 262 pp. (1934); (*b*) J. S. Machin and J. F. Vanecek, "Effect of Fluorspar on Silicate Melts with Special Reference to Mineral Wool," *Illinois State Geol. Survey Rept. Investigations*, No. 68, 15 pp. (1940); *Ceram. Abs.*, **22** [11] 192 (1943).

[1] H. F. Mulliken and W. J. Osborn, "Accuracy Tests of High-Velocity Thermocouple," p. 817 from chapter 9 of General Engineering, in Temperature, Its Measurement and Control in Science and Industry. Reinhold Publishing Corp., 330 West 42nd St., New York, 1941. 1362 pp.

[2] R. S. McCaffery and co-workers, "Determination of Viscosity of Blast-Furnace Slags, II," *Amer. Inst. Mining Met. Engrs. Tech. Pub.*, No. 383, pp. 27–54 (1931); *Ceram. Abs.*, **10** [3] 227 (1931).

The present studies undertake to measure the viscosity of that portion of the lime–magnesia–alumina–silica system which is liquid at temperatures of 1500°C. and lower, in the hope that the advantage gained in precision through the use of platinum-alloy viscometer parts and thermocouples may partly compensate for the shortened range. In this report, only compositions which contain 40% SiO_2 are considered. The field will be extended in a later report.

II. The Apparatus

The viscometer built for the present studies was intended to be usable over the range of temperatures in which platinum viscometer parts and platinum–platinum-10% rhodium thermocouples may be expected to have a reasonable life. No measurements were attempted above 1500°C. although occasionally the temperatures were increased to as much as 1550°C. to facilitate melting the charge.

The apparatus was similar to that designed by Nicholls and Reid[3] for use in the laboratories of the U. S. Bureau of Mines. It is of the oscillating or torsion pendulum type. Minor modifications in the lengths of the torsion wires and more convenient means for setting the vibrating system in motion have been incorporated in the apparatus used in the present study.

A shield has been added, which protects the mirror and inertia weight assembly from air currents. It was found that this improved the stability characteristics of the oscillating system.

The theory of the oscillating-type viscometer has been discussed at length by Rait,[4] Dantuma[5] and various others. The theory is not discussed here except in so far as is necessary to clarify certain points in the discussion of the calibration and the measurements.

The furnace (Fig. 1) is similar to that described by Nicholls and Reid.[3] A different method, however, was used to control the temperature. The voltage applied to the Globar tubular resistor was varied continuously rather than stepwise by means of a modified conventional-type potentiometer controller combined with a saturable reactor and a commercial electronic control panel described by the maker as a "thyratron reactrol heating control panel." This instrument is very flexible in its operation.

A Leeds and Northrup type K potentiometer and a platinum–platinum-10% rhodium thermocouple was used to determine the temperature of the melt. The location of this thermocouple is indicated in Fig. 1. The thermocouple was kept in contact with the bottom of the platinum crucible which held the melt. Figure 2 is a plot of variation of its e.m.f. readings taken over a period approximating that required to record data for a viscosity measurement. The temperature gradient from top to bottom in the melt was about 4°C., the bottom having the lower temperature. The gradient was affected by the position of the crucible relative to top and bottom of the furnace.

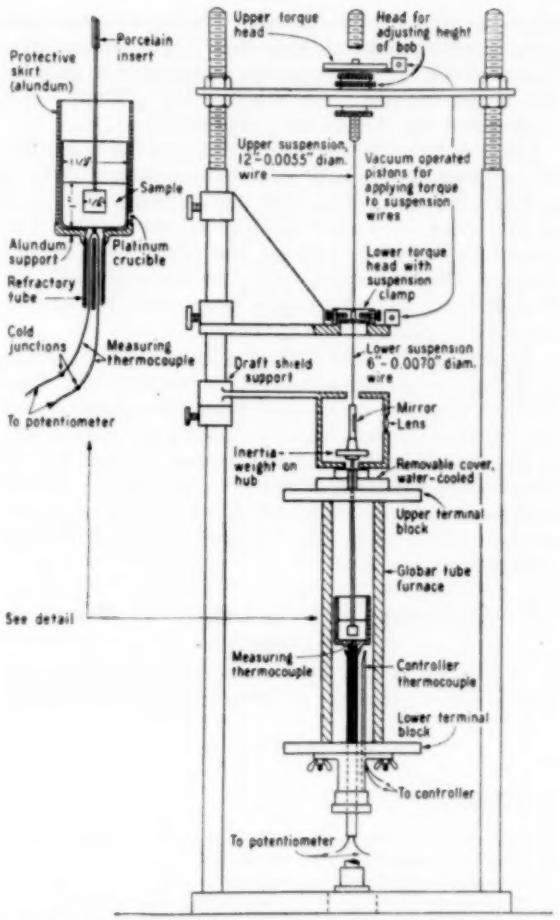


FIG. 1.—Schematic representation of viscosity apparatus; terminal blocks water cooled; lamp and scale placed approximately 5 ft. from mirror.

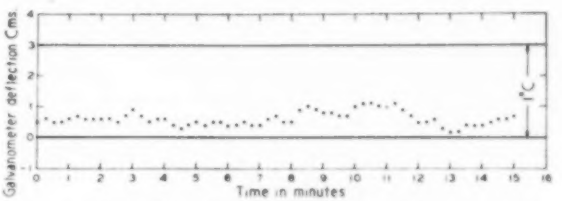


FIG. 2.—Variation of temperature with time at bottom of platinum crucible containing sample.

III. Preparation of Samples

The materials used were $Al(OH)_3$, $CaCO_3$, basic magnesium carbonate, and silica, all minus 200-mesh. All were analyzed, and account was taken of the analysis in determining the amounts weighed for the batches. The batch quantities were weighed and mixed in a

[3] P. Nicholls and W. T. Reid, "Viscosity of Coal-Ash Slags," *Trans. Amer. Soc. Mech. Engrs.*, **62** [2] 141–53 (1940); *Ceram. Abs.*, **19** [11] 255 (1940).

[4] J. R. Rait, "Viscosity of Slags and Glasses, I–III," *Bull. Brit. Refrac. Research Assn.*, No. 50 (June, 1939); reprinted in *Trans. Brit. Ceram. Soc.*, **40** [5] 157–204; [6] 231–69 (1941); *Ceram. Abs.*, **21** [1] 16 (1942).

[5] R. S. Dantuma, "Exact Determination of Coefficient of Internal Friction of Fused Salts," *Z. Anorg. Allgem. Chem.*, **175**, 1–42 (1928); *Ceram. Abs.*, **23** [3] 557 (1929).

tumbling jar for several hours. The mixture was then pressed into cylindrical briquettes, $1^3/_8$ in. in diameter, placed in the viscosity crucible, and melted in an electric muffle furnace. The crucible and contents were then cooled and the viscosity run made later.

For compositions containing considerable quantities of magnesia, a specially prepared mixture of $MgCO_3$ and SiO_2 was sintered, ground, and analyzed. Portions of this sinter were used to make up the batch. The reason for this was, of course, the bulkiness of the unsintered $MgCO_3$, which made it impossible to get enough batch in the crucible to produce the desired quantity of glass.

Enough batch was used to produce sufficient glass to stand approximately 1 in. deep in the crucible. This amount was fixed on because experiment showed that the center of the bob could be as much as $^1/_{20}$ in. above or below the center of the melt without causing serious error in the measurements if the melt was 1 in. deep, whereas the same amount of variation in placement of the bob would cause relatively large errors if the melt were only $^3/_4$ in. deep.

IV. Calibration and Evaluation of Instrument Constants

The motion of a mass oscillating as a torsion pendulum on the end of a wire is represented by equation (1).

$$I\frac{d^2a}{dt^2} + K\eta\frac{da}{dt} + Da = 0. \qquad (1)$$

a = angular deflection at any time.
t = time.
D = torque per unit angle of displacement which tends to restore system to rest position.
I = moment of inertia of system.
η = viscosity of medium in which mass is oscillating.
K = constant, characterized by shape and dimensions of bob and crucible.

The solution of equation (1) may take two forms, dependent on whether the inertia, I, or the damping effect of the medium dominates the motion; in other words, depending on whether the oscillating system is less than or more than critically damped. Convenient working forms of the solution corresponding to these two sets of conditions are given in equations (2) and (3).

$$\eta = \frac{DI}{EK\pi}\,\frac{\log_e p}{\left[1 + \left(\frac{\log_e p}{2\pi}\right)^2\right]^{1/2}} \qquad (2)$$

p is defined by $p = \frac{a_0}{a_1}$, where a_0 and a_1 are maximum deflections on the same side of the rest position on successive oscillations.
$\log_e p$ is called the logarithmic decrement.

$$\eta = \frac{D}{EK}\,\frac{(t_2 - t_1)}{\log_e a_1/a_2} \qquad (3)$$

Equation (3) is essentially that used by Lillie[6] for high viscosities.

a_1 and a_2 = angular displacements from rest position
E = correction factor to compensate for change in dimensions of bob and crucible with temperature.
$t_2 - t_1$ = time required for spindle to rotate through angle $a_1 - a_2$ in returning toward rest position after having been displaced.

D is dependent on the properties and dimensions of the torsion wire and may be determined from the period of oscillation T, once I is known, through use of the relation (equation (4)).

$$T = 2\pi\sqrt{\frac{I}{D}} \qquad (4)$$

The value of I, the moment of inertia of the system, is readily determined, as described by Lillie,[6] by using combinations of carefully made supplementary inertia weights, the moments of inertia of which can be calculated from their dimensions and masses.

Equation (4) neglects the damping effect of air. Allowance for this is made by applying a correction to $\log_e p$ in equation (2).

When D and I are known, the instrument constant, K, may be evaluated through calibration against a series of liquids of known viscosity, using equations (2) and (3). The liquids used were oils. The standards were standard viscosity samples, obtained from the National Bureau of Standards, and water. These were used to calibrate modified Ostwald-type viscometers, which were then used to determine the viscosity of the oils for calibrating the slag viscometer. The temperature of the oils was carefully controlled to ± 0.01°C. during the calibration runs. Since the calibration was at low temperature while the slag viscosity measurements were at high temperature, it was necessary to apply a correction for the change in dimensions of the platinum parts with temperature. This was done as follows:

The dimensions of the bob and crucible were assumed to enter into the value of K as a factor proportional to B, equation (5).

$$\frac{R_1^2 R_2^2 L}{R_2^2 - R_1^2} = B \qquad (5)$$

R_1 and R_2 = radii of bob and crucible, respectively.
L = height of bob.

Using the coefficients of linear expansion of platinum, values of B were calculated and the values of $B_T/B_0 = E$ were used as indicated in equations (2) and (3), B_1 and B_T being the values at 0°C. and at the temperature of measurement. An element of uncertainty is introduced into this correction by the fact that the bob was constructed from an alloy of 80% platinum and 20% rhodium. If the coefficient of linear expansion for this alloy is greatly different from that for platinum, the values of E are in error by a corresponding amount. It is, however, improbable that this amounts to more than a few percent of the total correction.

$E_{1200°C.} = 1.037$ $\qquad$ $E_{1500°C.} = 1.047$

The graph of the values of E versus temperature is nearly a straight line over this range.

As a check on the calibration, viscosity curves were run on a sample of glass kindly furnished by H. R.

[6] (*a*) H. R. Lillie, "Measurement of Viscosity by Use of Concentric Cylinders," *Jour. Amer. Ceram. Soc.*, **12** [8] 505–15 (1929).
(*b*) H. R Lillie, "Viscosity Measurements in Glass," *ibid.*, **12** [8] 516–29 (1929).

TABLE I

CALCULATION OF VISCOSITY

Melt No. 22-30 K = 10.81 $\log_{10} p$ air = 0.00099 CaO 35%–Al_2O_3 25%–SiO_2 40%

°C.	$\log_e p$ (corr.)	D	I	$1/E$	$\eta = \frac{\sqrt{DI}}{EK\pi} \frac{\log_e p}{\left[1+\left(\frac{\log_e p}{2\pi}\right)^2\right]^{1/2}}$	$\log_{10}\eta$
1500	0.43468	773.3	1788.8	0.955	1.43×10	1.155
1450	.65838	773.3	1788.8	.957	2.17×10	1.336
	$\frac{t_2 - t_1}{\log_e(a_1/a_2)}$				$\eta = \frac{D}{EK} \frac{(t_2 - t_1)}{\log_e a_1/a_3}$	
1400	4.2266	93.17		.959	3.49×10	1.543
1350	7.7237	93.17		.960	6.39×10	1.806
1300	15.474	93.17		.961	1.28×10^2	2.107
1250	34.100	93.17		.963	2.83×10^2	2.452
1200	11.784	773.3		.964	8.13×10^2	2.910
1150	38.114	773.3		.966	2.63×10^3	3.420
1100	164.41	773.3		.968	1.14×10^4	4.057

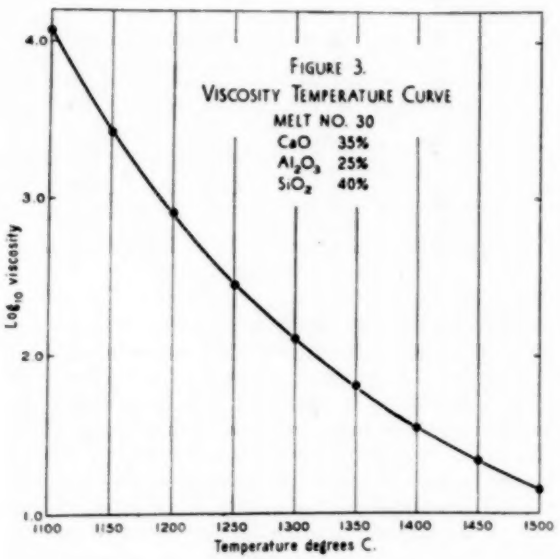


FIG. 3.

Lillie. The viscosity of this glass had been measured in his laboratory. The curves obtained on this glass with the apparatus used by the writers agree with those obtained in Lillie's laboratory, using apparatus of a different design, within 5°C. for any given viscosity.

V. Measurement of Viscosity

The design of the apparatus with two suspension wires results in four useful ranges. Two of these, for which equation (2) is used to calculate the viscosity, are employed over the ranges of 1 to 7 poises and 6 to 40 poises, respectively. The method used for these ranges is commonly referred to as the periodic decrement method. The other two useful ranges employ equation (3) for the calculation of viscosity and have lower limits of about 35 and 300 poises, respectively. There are no absolute upper limits. The precision of measurement is fairly satisfactory up to 10^6 poises and possibly higher. The method has been called the aperiodic method. All of the limits noted are practical limits imposed by choice of suspension wires and other factors and are not the absolute limits imposed by the mathematical and physical properties of the system.

The method of making an observation with the periodic decrement method is to record a series of maximum deflections to the right and to the left of the zero point as the system oscillates. The ratio of any maximum deflection to the next succeeding deflection on the same side is the basis for the determination of $\log_e p$. An even number of maximum deflections is averaged by means of the relation, equation (6).

$$p = (a_1/a_n)^{1/n} \qquad (6)$$

a_1 and a_n = initial and nth maximum deflections on same side of zero point.

Several such series are recorded and averaged. Any apparent drift in the value of $\log_e p$ is usually caused by the growth of crystals on the bob. The crystals have been observed many times when the bob was withdrawn from the melt and the furnace power was shut off as soon as drifts in the value of p were noted.

$\log_e p$, used in equation (2), is a corrected value obtained by determining the value of $\log_e p$ when the bob is oscillating in air and subtracting this value from that obtained when the bob is oscillating while immersed in the molten glass.

Observations, when the aperiodic method is used, consist in timing the transit between two values of the deflection, a_1 and a_2.

All values of a for both the periodic decrement method and the aperiodic method are expressed in angular units. A special logarithm table arranged to convert scale readings to $\log_{10} a$, where a is the deflection in minutes of angle, is convenient.

To illustrate the precision with which the data fit a smooth curve, the viscosity values for composition No. 22–30 are listed in Table I and plotted on Fig. 3. In obtaining these data, three of the four ranges of the viscometer were used.

VI. Viscosity Data

The compositions for which viscosity data are reported in this paper contain lime 15 to 45, magnesia 0 to 30, and alumina 5 to 30%. The increments in all cases were 5%, so that approximately that portion of the

TABLE II

VISCOSITY DATA

Lime–Magnesia–Alumina–Silica System (SiO_2 = 40%)

Melt No.	Composition (wt. %)			Viscosity (poises) at °C.					
	Al_2O_3	CaO	MgO	1500	1450	1400	1350	1300	1250
1–9	5	45	10	2.24					
2–40	5	40	15	1.99	2.61				
3–12	5	35	20	1.91	2.64				
4–45	5	30	25	1.90					
5–5	10	50	0	4.01	5.23	8.33			
6–6	10	45	5	3.29	4.60	6.77	10.27		
7–16	10	40	10	2.98	4.27	6.40	9.74		
8–41	10	35	15	2.62	3.64	5.26	8.31		
9–8	10	30	20	2.81	3.78	5.50	8.75		
10–47	10	25	25	2.46					
11–1	15	45	0	5.16	8.22	13.23	22.18	40.27	85.8
12–2	15	40	5	5.02	8.09	11.89	19.58	31.42	71.36
13–3	15	35	10	4.28	6.5	9.97	16.32	27.39	
14–42	15	30	15	3.72	5.33	8.02	12.73	22.07	59.28
15–4	15	25	20	3.84	5.55	8.34			
16–48	15	20	25	3.30					
17–21	20	40	0	8.32	13.69	21.48	35.07	67.56	147.9
18–50	20	35	5	7.69	11.26	17.92	29.43	55.50	115.73
19–15	20	30	10	6.94	10.04	15.15	24.76	44.30	98.2
20–43	20	25	15	5.61	8.37	12.83	20.74	35.29	74.63
21–14	20	20	20	5.41	7.70	12.50			
22–30	25	35	0	14.34	21.70	34.94	63.90	128.2	283
23–31	25	30	5	12.15	18.29	28.75	49.32	98.46	214.0
24–32	25	25	10	11.20	15.35	23.12	39.81	75.26	158.4
25–51	30	30	0	27.14	39.50	69.39	129.48		
26–52	30	25	5	18.94	30.40	51.37	96.0		
27–53	30	20	10	14.69	23.10	38.94	70.18		

compositional field which is molten at 1500°C. was covered at 5% intervals. The data are listed in Table II.

By graphic interpolation from the data of Table II, a table was built up for each temperature that listed those compositions for which the viscosity had constant values. These tables were used to prepare the triaxial diagrams of Fig. 4 (*a*), (*b*), (*c*), and (*d*), which show the variation of viscosity with composition at constant temperature.

The isokoms (lines of equal viscosity) roughly parallel the lines along which the acid-base ratios (moles SiO_2 + moles Al_2O_3) divided by (moles CaO + moles MgO) are constant. It is a noteworthy fact that, when the logarithms of the average viscosities along the lines of constant acid-base ratio are plotted against the acid-base ratios, the lines drawn through the points corresponding to the various temperatures seem to converge to a point where the acid-base ratio is approximately 0.5 and the viscosity has a very low value. Whether this holds for compositions other than those considered here must await further study.

The diagrams (Fig. 4) are comparable with those presented by McCaffery,[7] but there are important differences as will be seen when Fig. 4 (*a*) is compared with McCaffery's diagram for the same temperature and the same compositional range. McCaffery shows lines indicating viscosity values in regions where the present writers were unable to melt the samples at the temperatures in question. This probably means that McCaffery's samples, which were cooled from a higher temperature, in such instances were supercooled as was also the case with many samples in this study. In other instances, it is suspected that disagreement between these data and McCaffery's may be due to the presence of crystals in his molten samples. If crystals appear in quantity, the composition of the liquid portion of the sample may of course be far different from that of the sample as a whole, and the apparent viscosity observed would not represent the viscosity of the sample but that of the liquid portion modified to an unknown degree by the effect of the suspended crystals. Anorthite crystallizes readily from melts in parts of the compositional region under consideration. This removes SiO_2 and Al_2O_3 from the melt out of proportion to the CaO removed and would cause apparent reduction in the viscosity.

In the present studies, following a lowering of the temperature, changes in viscosity were never observed through more than a few minutes after the new temperature became constant in any melt in which there was no evidence of the presence of crystals. In order to detect any drift in the value of the viscosity, three series of measurements were made at each temperature.

The sensitivity of the apparatus to the appearance of crystals is a fortunate circumstance in that it frequently prevents the recording of misleading viscosity values. When platinum alloy crucibles and bobs are used with samples of the compositions employed in this study, crystals usually appear first either on the bob or on the crucible wall. If they appear on the bob, their presence is almost immediately revealed as an apparent change in the viscosity. It is probable that

[7] R. S. McCaffery and co-workers, "Determination of Viscosity of Blast-Furnace Slags, I," *Amer. Inst. Mining Met. Engrs. Tech. Pub.*, No. 383, pp. 1–27 (1931).

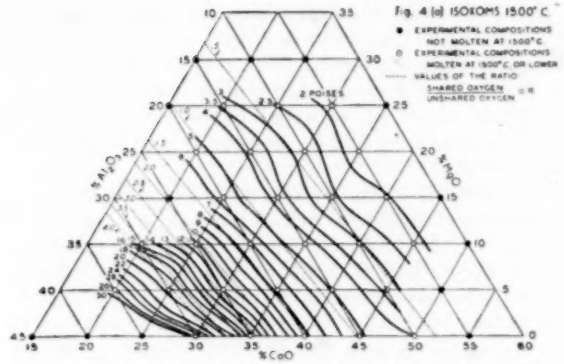


Fig. 4 (a) ISOKOMS 1500° C.
EXPERIMENTAL COMPOSITIONS NOT MOLTEN AT 1500° C.
EXPERIMENTAL COMPOSITIONS MOLTEN AT 1500° C. OR LOWER
VALUES OF THE RATIO SHARED OXYGEN / UNSHARED OXYGEN
2 POISES
% Al_2O_3
% MgO
% CaO

FIG. 4 (*a*).—Variation of viscosity with composition at constant temperature; solid lines are 1500°C. isokoms, (lines along which viscosity is constant).

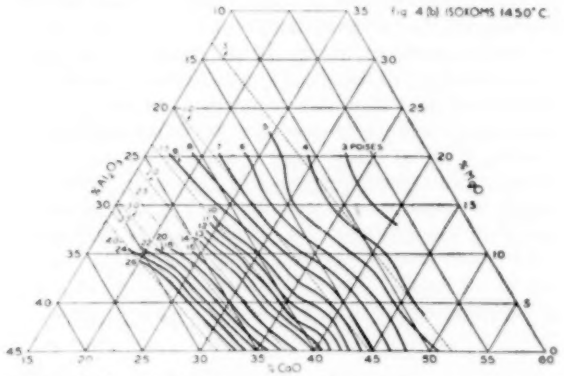


FIG. 4 (*b*).—Variation of viscosity with compositions at constant temperatures; solid lines are 1450°C. isokoms, (lines along which viscosity is constant).

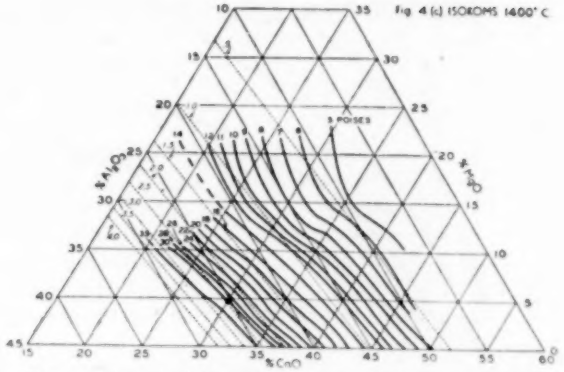


FIG. 4 (*c*).—Variation of viscosity with composition at constant temperatures; solid lines, 1400°C. isokoms, (lines along which viscosity is constant).

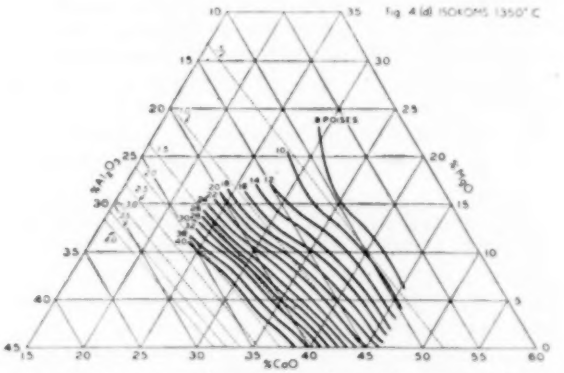


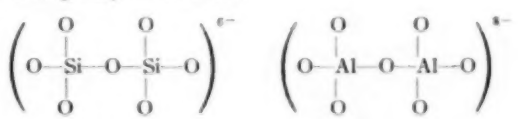
FIG. 4 (*d*).—Variation of viscosity with composition at constant temperature; solid lines are 1350°C. isokoms, (lines along which viscosity is constant).

the growth of crystals on the crucible wall has a similar but less marked influence on the motion of the bob.

VII. A Theory of Effect of Composition on Viscosity of Melts Containing SiO_2 and Al_2O_3

Postulate: The most effective way to cause increased viscosity at constant temperature is to increase the number and size of the large molecules or ions present and vice versa.

Let it be assumed that, provided there is enough basic oxide present to furnish the required oxygen, silicon and aluminum can exist in the melt as SiO_4^{4-} ions and AlO_4^{5-} ions. If the basic oxides present are less than enough to furnish this much oxygen, then instead of SiO_4^{4-} and AlO_4^{5-}, polymeric ions such as the following may be formed:



As the amount of basic oxides present decreases, the lengths of the chains increase. They branch and eventually extend into three dimensions, forming the networks postulated by Zachariasen.[8] Silicon and aluminum atoms may form units of the same chain or network. The relation between the number of oxygen atoms present and that of silicon and aluminum atoms present will be called the oxygen-silicon ratio. It is understood that, in calculating this ratio, each aluminum atom is counted as a silicon atom. For monomer ions, the oxygen-silicon ratio would be 4; for chains of infinite length, it would be 3; and for three-dimensional networks of infinite extent, it could be as low as 2.

The oxygen atoms, which act as bridges between silicon or aluminum atoms, are called shared oxygen atoms. The ratio of shared to unshared oxygen atoms, which will be called R, is a measure of the degree of polymerization. R is calculated from the oxygen-silicon ratio, N, by means of the relation (equation (7)).

$$R = (4 - N)/2(N - 2) \qquad (7)$$

This relation is easily derived from consideration of the situation of a central silicon atom surrounded by 4 oxygen atoms. Unclosed chains of n silicon atoms, whether they be straight or branched, have $2n + 2$ unshared oxygen atoms and $n - 1$ shared oxygen atoms. R approaches 0.5 as n approaches infinity.

[8] W. H. Zachariasen, "Atomic Arrangement in Glass," *Jour. Amer. Chem. Soc.*, **54** [10] 3841–51 (1932); *Ceram. Abs.*, **12** [4] 145 (1933).

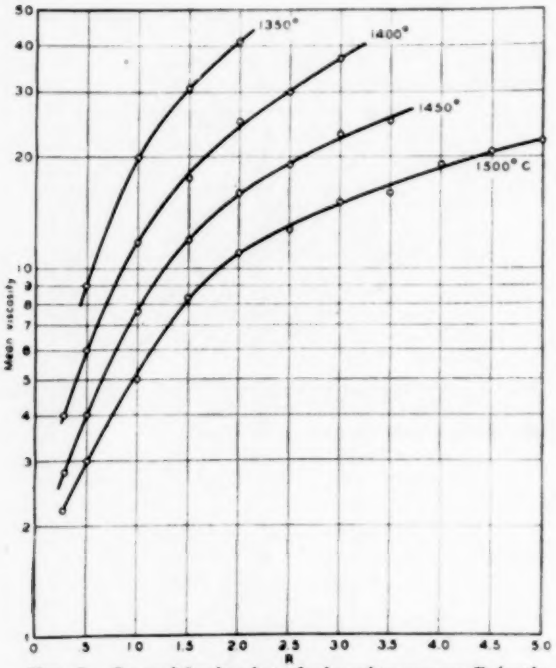
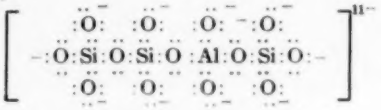


FIG. 5.—Logarithmic plot of viscosity versus R (ratio of shared oxygen to unshared oxygen); viscosities are estimated average values along constant R lines.

Values of $R > 0.5$ would be associated with cross linkage between chains.

Consideration of the electronic formula of a polymeric ion containing aluminum and silicon atoms indicates that the substitution of aluminum for silicon, atom for atom, increases the negative valence of a chain ion by one for each atom substituted without changing the length of the chain. The reason, of course, for this relation is that the aluminum atom has only 3 electrons in its outer shell whereas the silicon atom has 4. An aluminum-bearing glass, therefore, should tolerate more alkaline atoms than an all-silicate glass and still have only slightly lower viscosity than the all-silicate analog. There is of course a limit to the amount of alumina which can be substituted for silica since all-aluminate glasses are not known. A chain of aluminum atoms with no silicon atoms would probably be unstable.



The probability of a high percentage of large particles (polymeric ions) would be increased then by increasing the percentage of alumina and/or silica and decreased by increasing the percentage of lime and/or magnesia. Magnesia might be expected to be somewhat more effective than lime due to the smaller size of the magnesium ion.

The pattern of the system of isokoms at constant temperature should be relatively simple; that is, a system of lines without sharp changes of direction which at low and moderate viscosities would roughly parallel the lines of constant value of R.

The isokoms might be expected to vary to a degree from parallelism with the constant R lines. Qualitatively, this variation should be related to the relative amounts of lime and magnesia present. Substituting MgO for lime should result in lower viscosity so that on the high magnesia end of the constant R lines the isokoms should depart from the R lines to the left and on the low magnesia end they should depart to the right. It must be kept in mind, however, that an equilibrium process is under consideration in which the rates of polymerization and depolymerization are important factors.

Some of these lines along which R is constant are drawn on the triaxial diagrams of Fig. 4. The lines are roughly parallel to the isokoms for low and moderate values of the viscosity, but the fit is not so good at higher viscosities. Figure 5 shows the variation of log viscosity with R. The viscosities used are averages as estimated from Fig. 4 along lines where R is constant.

VIII. Summary

The viscosities of those compositions in the CaO–MgO–Al_2O_3–SiO_2 system which contain 40% SiO_2 and which are liquid at 1500°C. have been measured. The isokoms are roughly parallel to the lines along which the ratio of acidic components to basic components is constant. A theory of the variation of viscosity with composition based on the assumption of polymeric silicate ions is proposed.

Acknowledgment

The writers wish to acknowledge their indebtedness to R. E. Grim for petrographic examination of crystalline material from certain melts and to W. F. Bradley for certain X-ray analyses.

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NICKEL FLASHING AND ITS RELATION TO ENAMEL ADHERENCE*

By Eugene Wainer and W. J. Baldwin

Abstract

Nickel flashing as applied to enameling stock is shown to be primarily metallic nickel. The role of nickel in developing enamel adherence is apparently bound up with the retardation of oxidation which the nickel flash imparts in the enameling cycle. The problem of adherence may be considered to be a corrosion phenomenon of the base iron developed by the action of gases and other agents which may be present at enameling temperatures. As such, the degree of adherence is a function of oxygen pressure at the interface when the glass is fused. The equilibria developed are strongly affected by the presence of nickel.

Using cover coats directly on iron, the amount of nickel required will vary with each particular enamel composition. Some evidence as to the nature of the adherence-promoting oxide is presented.

I. Introduction

The development of enameling steels[1] suitable for application of white enamel on steel without the use of ground coat has strongly emphasized means of obtaining glass-metal adherence without the use of dark-colored cobalt enamels. One method which can be used is the application of nickel coating on the iron in the pickle system. Such procedures involve the deposition by galvanic methods.[2] The properly cleaned stock is immersed in a weakly acid, buffered solution of the sulfate, chloride, or nitrate of nickel at high temperatures and for periods ranging from 1 to 10 minutes.

Most references to nickel flashing deal with the proper mechanics of application. Very little information is available as to the role of nickel in the adherence phenomenon. The evaluation of this feature is the purpose of the present paper.

II. Experimental Studies

(1) Nature of Nickel Flash

An acid-pickled, clean, oxide-free surface of a sheet of nickel was completely immersed and heated for periods ranging from several minutes to hours in a 1 to 1 solution of concentrated NH_4OH. No nickel was dissolved as determined in the usual fashion with dimethylglyoxime. This insolubility of metallic Ni in ammonia is also pointed out in the literature.[3] The freshly precipitated hydrates, oxides, and other compounds of Ni are known to be quite soluble in ammonia[4]

* Forty-Seventh Annual Program, 1945, The American Ceramic Society (Enamel Division, No. 10). Received May 29, 1945.

[1] G. F. Comstock and E. Wainer, "New Titanium Steel for Vitreous Enameling," *Iron Age*, **155** [7] 60 (1945).

[2] (*a*) C. D. Clawson, "Adherence of Ground Coats to Sheet Steel," *Ceram. Ind.*, **13** [2] 164–66 (1929); Enamel Bibliography, 1944 ed., p. 48.

(*b*) "Bath of Adhering Oxides for Sheet-Iron Enamels," *Glashütte*, **66** [35] 606–608 (1936); Enamel Bibliography, 1944 ed., p. 22.

(*c*) G. W. Hofstetter, "Nickel Bath in Pickle Room?" *Better Enameling*, **3** [12] 9–10 (1932); *Enamelist*, **12** [1] 15–16 (1934); Enamel Bibliography, 1944 ed., pp. 122–23.

(*d*) H. L. Cook, "Metal Preparation for Vitreous Enameling," *Ceram. Forum*, **1** [10] 2 (1935); Enamel Bibliography, 1944 ed., pp. 53–54.

(*e*) J. E. Hansen and J. T. Irwin, "Nickel Dip in Enameling Practice," *Jour. Amer. Ceram. Soc.*, **18** [8] 225–29 (1935).

(*f*) F. R. Porter, "Physics and Chemistry of Nickel Pickling," *Better Enameling*, **4** [1] 18–19 (1933); Enamel Bibliography, 1934, ed., p. 218.

(*g*) W. J. Baldwin, "Cleaning Steel Prior to Enameling," *Metal Cleaning & Finishing*, **8** [7] 429–34; [8] 465–68 (1936); Enamel Bibliography, 1944 ed., pp. 19–20.

(*h*) "Special Pickling Process," *Emaillerie*, **4** [7] 13–16 (1926); Enamel Bibliography, 1944 ed., p. 255.

(*i*) M. J. Bozsin, "Setting up Pickling Control Laboratory and Method for Testing Solutions," *Enamelist*, **14** [3] 9–15 (1936); Enamel Bibliography, 1944 ed., p. 33.

(*j*) James Pettyjohn, "Nickel-Dip Treatment of Enameling Iron," *Metal Cleaning & Finishing*, **9** [12] 995–98 (1937); Enamel Bibliography, 1944 ed., p. 212.

(*k*) H. L. Cook, "Advantages of Nickel-Dip Solution in Modern Pickle Rooms," *Enamelist*, **15** [7] 5–7 (1938); *Ceram. Abs.*, **19** [4] 86 (1940).

(*l*) J. M. Zander, "Factors Affecting Rate of Nickel Depositions in Nickel Pickling," *Better Enameling*, **9** [6] 5–8 (1938); *Ceram. Abs.*, **19** [8] 183 (1940).

(*m*) E. P. Poste, "Chemistry and Vitreous Enamels," *Ind. Eng. Chem.*, **32** [1] 9–15 (1940); *Ceram. Abs.*, **20** [1] 7 (1941).

(*n*) "Nickel Dip in Enameling Plants," *Ceram. Ind.*, **34** [6] 52–54 (1940); *Ceram. Abs.*, **19** [8] 184 (1940).

(*o*) "Pickling Aids in Enameling Plants," *Glashütte*, **71** [4] 41–42 (1941); *Ceram. Abs.*, **20** [7] 165 (1941).

(*p*) W. B. Felter, "Reclaim of Nickel-Dip Solutions," *Enamelist*, **19** [5] 5 (1942); *Ceram. Abs.*, **21** [8] 165 (1942).

(*q*) W. A. Wesley and H. R. Copson, Coating Steel with Nickel by Chemical Replacement. Research Laboratory, International Nickel Co., Inc., Bayonne, N. J. (prepublication copy).

(*r*) H. W. Alexander and R. S. Sheldon, "Nickel Plating on Iron by Immersion," U. S. Pat. 2,265,467, Dec. 9, 1942.

(*s*) L. D. Hammond, "Boric Acid Buffer," *Trans. Amer. Elec. Soc.*, **30**, 103, 201 (1916); **45**, 219 (1924).

(*t*) C. D. Hodgman, Handbook of Chemistry and Physics, p. 420, 27th ed. Chemical Rubber Co., 1943.

[3] A. J. Hale and H. S. Foster, "Insolubility of Nickel in Ammonia," *Jour. Soc. Chem. Ind.*, **34**, 464 (1915); see J. W. Mellor, Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. XV, pp. 152 and 167. Longmans, Green, & Co., 1936.

[4] R. Tuphuti, "Solubility of NiO in Ammonia," *Ann. Chim. Phys.*, [2], 78, 133 (1840); [2] 79, 153 (1841); see J. W. Mellor, Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. XV, pp. 380–81. Longmans, Green, & Co., 1936.

TABLE I

CONDITIONS OF PICKLING PROCEDURE

Run No.	pH	Ni flash (minutes)	Total Ni (gm./sq. ft.)	NH_4OH at room temp.		NH_4OH at 350°F.	
				Insoluble	Soluble	Insoluble	Soluble
1	6.2	1	0.016	0.014	0.002	0.014	0.002
2	"	3	.083	.073	.010	.326	.047
3	"	5	.166	.160	.006	.146	.020
4	3.6	2	.063	.062	.001	.033	.031
5	"	4	.066	.058	.008	.025	.041
6	"	6	.097	.091	.006	.051	.046
7	6.2	2	.064	.055	.009	.055	.009
8	"	3	.062	.058	.004	.058	.004
9	"	4	.144	.142	.002	.142	.002

so that the ammonia-partition test represents a method for determining the presence and amount of metallic nickel on an iron base, providing the samples have not been heated at high temperatures. A photomicrographic cross section at high magnification also determines whether the nickel is metallic in nature, while electron-diffraction patterns,[5] when obtainable, are absolute from an identification standpoint.

Several 4- by 6-in. 20-gauge titanium steel sheets[1] were pickled in accordance with a given schedule. A c.p. grade of chemicals and distilled water were used throughout; the pickle-bath containers were glass beakers, and the temperatures were controlled within ±5°F. The stock was suspended in the baths with glass string to eliminate contamination by foreign metal. The pickle schedule for the sheets, which were completely free of scale or rust, was as follows:

(1) Soak in carbon tetrachloride for 3 minutes, air dry.
(2) Treat 5 minutes in bath at 165°F. containing 150 cc. *N* brand sodium silicate* in 3 liters of water; rinse in hot water at 176°F.
(3) Acid pickle 5 minutes at 160°F. in bath containing 100 cc. of 66° Bé H_2SO_4 in 3 liters of water; rinse in hot water, 176°F.
(4) Nickel flash; bath consists of 60 gm. of nickel ammonium sulfate and 15 gm. of boric acid dissolved in 3 liters of water at 176°F.; time and pH are indicated in Table I; rinse in hot water, 176°F.
(5) Neutralize in bath containing 10 gm. of NaCN in 3 liters of water for 2 minutes at 160°F.; air dry without washing unless otherwise indicated.

Before using the baths, the solutions were tempered by placing steel sheets in each bath at its usual temperature for one-half hour. Three 4- by 6-in. test sheets were pickled as indicated by the schedule and according to the conditions detailed in Table I. The pickle schedule was followed in detail except for the rinse in (7), (8), (9) in Table I. These plates were thoroughly washed in running water for several minutes before drying. Each test sheet was then cut lengthwise into four strips. The total nickel was determined on one strip after treatment with nitric acid; the amount of soluble nickel on a second strip was determined by the ammonia-partition method; the third strip was heated at 350°F. for 6 hours; and the last strip was heated at 1000°F. for 6 minutes. The soluble-insoluble nickel was determined in each case by the ammonia-partition procedure. The results are given in Table I. The room-temperature results indicate that the deposit is primarily metallic in nature. The slight amount of ammonia-soluble nickel is probably due to subsequent corrosion or drag out. A comparison of runs Nos. 7, 8, and 9 with Nos. 1 to 6 (Table I) at 350°F. indicates that small amounts of corrosive agents, probably sulfates, will oxidize the nickel. Adequate rinsing between nickel flash and neutralizer is thus indicated as a requirement.

After heating at 1000°F., the nickel was completely insoluble in ammonia. Judging from its appearance and its ammonia insolubility, complete oxidation evidently had occurred. Section II, (4) and (7), shows that the metallographic and electron-diffraction evidence supports the conclusion that the deposit is metallic nickel. Electrochemically, it is difficult to see how it can be anything other than metal.

(2) Nature of Nickel and Adherence

A second 4- by 6-in. test panel was treated at the same time and by the same method as described in section (1). Duplicate strips were enameled with (*a*) an antimony-free zircon enamel and (*b*) a zircon-free, high antimony enamel. The adherence usually dropped as the amount of ammonia-soluble nickel increased. All adherence was lost after the 6-minute, 1000°F. treatment except for No. 9. A major amount of adherence was retained in No. 9 but to a lesser extent than with the low-temperature specimens.

It may be concluded that oxidation of a nickel-flashed specimen by heat before enameling is to be avoided.

According to the handbooks, metallic nickel is oxidized in excess of air or oxygen to NiO on heating to 752°F. (400°C.); at 400°C., NiO is oxidized to Ni_2O_3, which is stable to 600°C. (1112°F.). Above 600°C., Ni_2O_3 will change to Ni_3O_4, most probably through the reaction $NiO + Ni_2O_3 \rightarrow Ni_3O_4$. Thus it is possible that a combination of all the oxides of nickel are present at one time or another in the heating-up cycle. The effect of the presence of iron and its compounds on the nature of the nickel oxide present will be discussed in part III.

(3) Amount of Nickel vs. Adherence

A number of nickel-flashed panels were prepared so as to present a continuous series from 0.012 to 0.260 gm. per sq. ft. These panels were enameled with a zircon-type, antimony-free enamel and also with a

[5] H. R. Nelson, "Metallurgical Applications of Electron Diffraction," *Jour. Applied Physics*, **9** [10] 623–27 (1938).
* Philadelphia Quartz Co., Philadelphia, Pa.

TABLE II

RESULTS OF ANALYSES BY NICKEL FLASHING

Plate No.	Addition salt	pH		Flash (minutes)	Ni (gm./sq. ft.)		
		Start	Finish		(a)	(b)	(c)
1	None	6.0	4.8	5	0.09	0.18	0.06
2				10	.14	.15	.07
3				20	.16	.16	.12
4	NaF	6.0	6.0	5	.09	.08	.09
5				10	.14	.14	.15
6				20	.21	.22	.21
7	Na_2SiF_6	6.0	5.9	5	.07	.08	.07
8				10	.13	.13	.14
9				20	.21	.21	.20
10	NaCl	6.0	4.7	5	.08	.10	.06
11				10	.15	.14	.15
12				20	.16	.16	.15
13	$Na_2C_2O_4$	6.0	5.9	5	.06	.08	.06
14				10	.07	.08	.07
15				20	.12	.10	.09

zircon-free, high antimony-type enamel. The zircon enamels were of the conventional type, fired at 1540°F. for 3 minutes; the antimony enamels were acid resisting and non-acid resisting, both fired at 1520°F. for 3 minutes.

The zircon enamels developed adherence at a nickel content of 0.025 to about 0.10 gm. per sq. ft., the optimum approximating 0.05 gm. per sq. ft. The antimony enamels developed adherence at 0.025 to about 0.15 gm. per sq. ft., some adherence still developing at 0.21 gm. per sq. ft. The optimum appears to be about 0.08 gm. per sq. ft. The fact that the nickel range is broader and that the amount of nickel required is higher in the case of the adherence-promoting antimony enamel is significant. To insure adherence for the zircon enamels, close control of the nickel flash is required. With any enamel, adherence can be destroyed by the deposition of too much nickel.

(4) Control of Rate of Ni Deposition

As shown by Zander,[2(f)] a variety of factors must be controlled in order to obtain the stated amount of nickel in the flashing cycle. These factors generally are time, temperature, hydrogen-ion concentration, age of bath, and cleanliness. In spite of such control, the deposition is often erratic from plate to plate and even on the same plate. The nonuniformity of the deposition is evident in Table I. Wesley and Copson[2(g)] reduce the effect of variations in hydrogen-ion concentration by using highly concentrated baths of $NiCl_2$, but such concentrations (80 oz. per gal.) are not common in the enameling industry. They point out that previous treatment of the steel before nickel flashing is an important variable and that a sulfuric acid pickle shortly before immersion in the nickel bath results in an uneven sporadic nickel coating, presumably because the sulfuric acid pickling forms large anodic areas. They recommend a pumice scrub followed by cathodic cleaning in caustic. The porous nature of the nickel deposit is emphasized by these same authors.

In view of the almost universal use (by enamelers) of H_2SO_4 pickle just before nickel flashing, anodic passivity is probably the cause of the sporadic nature of the deposition which is so frequently encountered. The evidence is fairly good that the rate of nickel deposition will depend on the nature of the steel and on its previous treatment.

The galvanic deposition of nickel by flashing is essentially a corrosion mechanism. The iron goes into solution through acid action; a cathodic area is developed adjacent to the pit formed; and metallic nickel is deposited on the cathodic area, the region where the iron first dissolved being anodic. Concentration depolarization, through starvation of acid or nickel at the steel surface, may thus be another factor in control which can be easily overcome by agitation of the solution or movement of the work.

Relative to anodic passivity, it is interesting to note that the electroplater encounters the same difficulty, which he surmounts by the use of fluoride ion.[6]

The use of baths of fluoride and other ions was investigated; five baths in all were prepared by adding fixed amounts of salts to the nickel flash (section II (1)). The salts were NaF, Na_2SiF_6, NaCl, and $Na_2C_2O_4$; 15 gm. of each salt were added to separate nickel baths. In each case, the starting hydrogen-ion concentration was adjusted to 6.0 at 180°F. The bath was tempered, in each case, at full temperature with 1 sq. ft. of steel surface for one-half hour before use. The nickel-flashed plates were analyzed and photomicrographs were made. The flashing was done in triplicate but not all of the plates were analyzed. The results are shown in Table II.

Both the oxalate and the fluosilicate developed voluminous flocculant precipitates. Fluoride ion stabilizes the rate of deposition of nickel (at least in a relatively

[6] (*a*) D. W. Robinson, "Mg Sulfate in Nickel Plating Solutions," *Metal Ind.* [New York], **14,** 287 (1916); "Mechanical Plating," *ibid.*, **15,** 61–64 (1917).

(*b*) W. Blum, "Use of Fluorides in Solutions for Nickel Deposition," *Trans. Amer. Electrochem. Soc.*, **39,** 459–82 (1921).

(*c*) M. Schade, "Über die Polarization Nickel. Dissertation, Univ. of Leipzig, 1912.

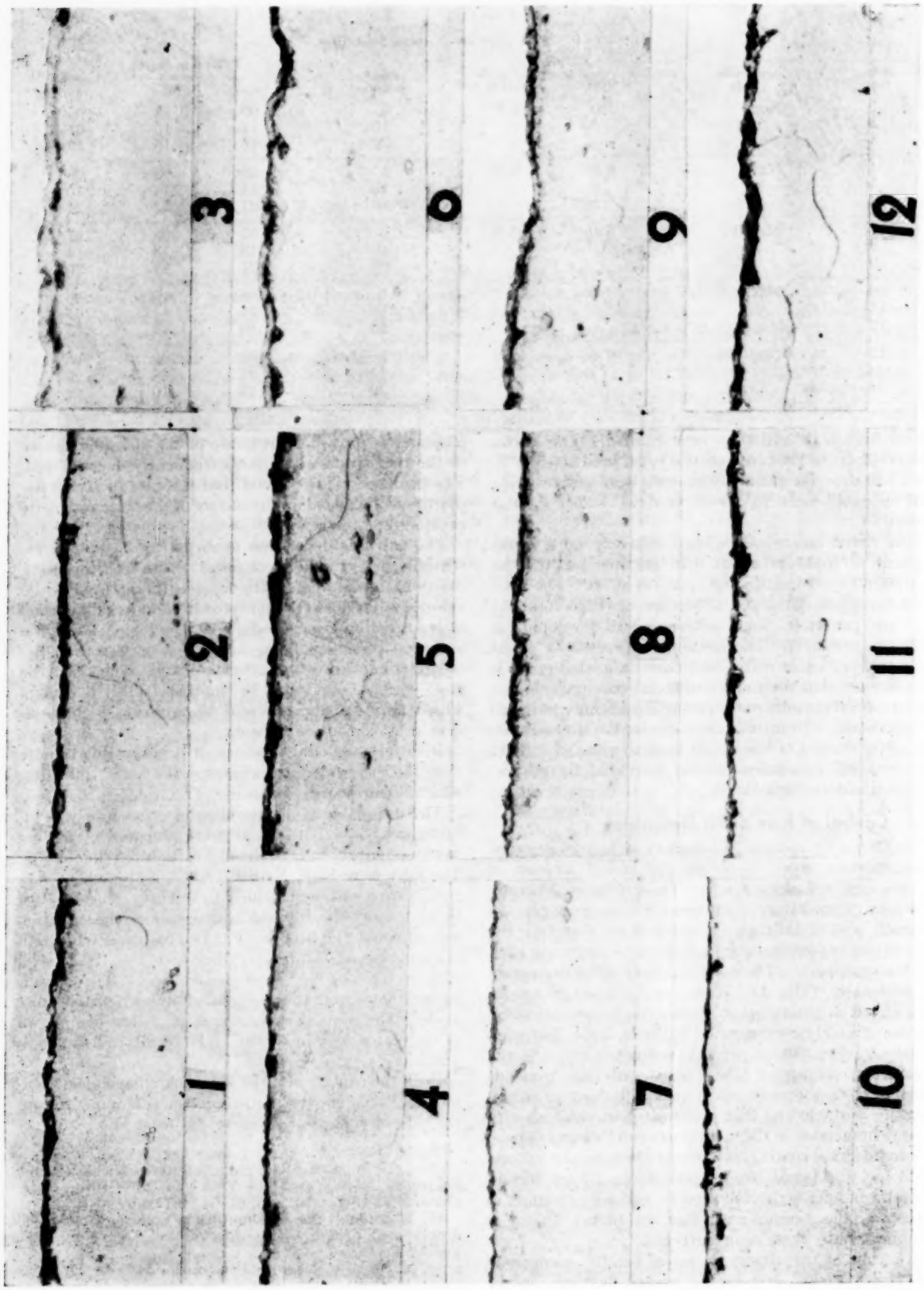

FIG. 1.—Cross sections of nickel-flashed specimens (↑ × 1414 → × 1000)

new bath) with the steel used,[1] and its use is therefore recommended. The effect on stabilization of hydrogen-ion concentration, which may be due to the formation of fluoborates in the bath, should also be mentioned.

Photomicrographs of some of these nickel-flashed specimens are shown in Fig. 1. The nickel content of these specimens is given in column (*a*) of Table II. The sections of the oxalate ion bath are omitted because good photographs could not be obtained. The magnification in the up-and-down direction is approximately 1414 times while the crosswise magnification is about 1000 times. The coating in all cases, after polishing and examination under the microscope, has the typical appearance of metallic nickel.*

The differences in behavior are evident. The straight sulfate bath tends to deposit rather coarse crystals of nickel in the initial and vital stages, whereas the halide-treated baths appear to develop rather fine and relatively evenly distributed crystalline deposits. A black smudge (apparently copper sulfide) tends to deposit along with the nickel in the early stages in the case of the sulfate and chloride but is almost absent in the case of the fluoride and fluosilicate. Elimination of codeposition of the black smudge may be a factor resulting in the superior behavior of the fluoride baths. Cleanliness plus crystal fineness plus elimination of passivity plus stabilization of the hydrogen-ion concentration are advantages of the fluoride-treated baths over the normal sulfate type.

(5) Effect of Nickel Coating on Oxidation Rate of Base Iron

Wesley and Copson[2(q)] indicate that the nickel coating is porous and that the base iron, when coated with such porous nickel, rusts at room temperature about as rapidly as when no nickel is present. This observation refers to relatively lengthy corrosion periods where diffusion time for the corrosive agent is ample for equilibrium.

To determine the effect of Ni with conditions similar to those met in enameling practice, the nickel content of several samples flashed in different baths and at different times were determined, and 1-in. squares were cut in such fashion as to eliminate finger contact. These squares, plus a blank, were weighed accurately on a chemical balance. Pieces were then heated for 2 minutes at 1200° to 1600°F. The results are recorded in Table III.

The results indicate that the oxidation of the system is restricted and reduced by the presence of nickel as a coating and that such restrictive action is proportional to the continuity and thickness of the nickel coating. While the restrictive role of the nickel appears to be general over the entire temperature range, such restriction of oxidation in the sulfate and oxalate baths is somewhat more pronounced (*a*) above 1400°F. than (*b*) below 1400°F.; the rate of oxidation, in the fluoride and fluosilicate is (*c*) retarded up to 1400°F., (*d*) increased more rapidly than normal between 1400° and 1500°F., and (*e*) slowed again above 1500°F. The photomicrographs ((4) through (9) in Fig. 1) for the (*d*) and (*e*) results indicate that the deposit is cleaner than in the other reactions.

TABLE III

EFFECT OF NICKEL COATING ON OXIDATION RATE OF BASE IRON

Specimen No.*	Weight increase (%) at °F.				
	1200	1300	1400	1500	1600
Blank	0.002	0.039	0.075	0.149	0.271
1-a	.004	.030	.104	.143	.233
2-a	.015	.020	.094	.127	.190
3-a	.013	.026	.053	.101	.152
4-a	.000	.023	.062	.097	.185
5-a	.000	.011	.037	.133	.164
6-a	.002	.004	.026	.080	.142
13-a	.001	.027	.087	.149	.191
14-a	.002	.034	.076	.117	.184
15-a	.000	.007	.050	.104	.189
7-a	.003	.023	.096	.134	.201
8-a	.003	.011	.029	.083	.122
9-a	.002	.011	.042	.055	.106

* From Table II.

(6) Effect of Nickel on Oxide Formed on Iron

Nickel coating has been shown to retard the rate of oxidation of iron at high temperatures in air (see section II (5)). For adherence purposes, knowledge of the nature of the oxides formed is of vital importance. Experiments were undertaken relating to the nature of the oxides formed in order to obtain data on adherence.

Sheets of clean, well-pickled enameling iron of the type previously mentioned[1] were heated in an oxidizing atmosphere at temperatures ranging from 1000° to 1600°F. for periods ranging from 3 seconds to 3 minutes.

Every range of oxide coating was obtained from an invisible film to a film comparable in thickness to the wave length of light (as indicated by interference colors), to relatively thick black coatings, and finally to coatings which were quite thick and velvety black in appearance. Without exception, no adherence was observed on any of these specimens with the zircon-type enamel.

Electron-diffraction studies[7] have shown that the exterior portions of the oxide film formed are, in every case, α-Fe_2O_3. It is therefore evident that α-Fe_2O_3 is not the adherence-promoting oxide, at least when formed by preoxidation procedures. The nickel-flashed specimens behaved in a somewhat similar fashion on the basis that preheating in air at 1200°F. or above always reduced or eliminated the degree of adherence obtained. The reduction in degree of adherence was minor, however, if the heating was done for a few seconds only at 1000° to 1200°F. Microscopic examination of the nickel-flashed steels before enameling showed that the

* The magnification in the up-and-down direction is apparently different from the crosswise direction since the metal specimen was cut at an angle of 45 degrees through the surface film. In effect, this view is spread according to the ratio of the hypotenuse of a triangle to one of the sides or 1.414 (the sides of the right triangle being equal in length in this case).

[7] Shizuo Miyake, "Study of Oxide Films on Metal Surface with Cathode-Ray Diffraction (II) Fe, Cr, Ni, and Their Alloys," *Sci. Papers, Inst. Phys. Chem. Research* [Tokyo], **31**, 161–73 (1937); *Chem. Abs.*, **31**, 4244 (1937). See also Nelson, footnote 5.

iron was oxidizing under the nickel coat, and when such oxide was thick enough it penetrated and pushed off the nickel coating in flakes.

If the heavy scale formed by prolonged oxidation (several minutes to hours) is chipped off and examined, the oxide on the inner surfaces is found to be Fe_3O_4 or magnetite.* The question of the nature of heat-formed oxides of iron will be discussed in section III.

Samples of steel were heavily nickel flashed,[2(g)] using nickel chloride baths, and then bright annealed to form a tight continuous film of iron-nickel alloy on the surface. These sheets as well as sheets of Invar (an N alloy containing 36% Ni) were enameled under various conditions.

Both types of stock were enameled with a high antimony enamel and a zircon antimony-free enamel. Adherence was uniformly good on the antimony enamel and nil on the zircon type. A significant feature on the zircon enamel showed up at the interface between the glass and metal. No oxide developed on the metal surface and no appreciable amount of oxide dissolved in the glass. After fracture, the metal surface was clean and bright, and the inner glass surface against the metal was almost white with a faint greenish tinge. (Incidentally, the usual color of the interface bond on a nickel-flashed specimen showing good adherence with a zircon enamel containing no adherence-promoting oxide is gray-green at the metal-glass interface, shading to green as the solution of oxide progresses into the glass.) The enameling operation thus protects the surface of the metal through the enameling temperature range.

The nickel samples and Invar stock were then heated in air before enameling at 1400°, 1475°, 1500°, 1525°, 1550°, and 1600°F. for 3 minutes, and a visible blue-black scale developed. These scaled plates were enameled with a zircon enamel. Good adherence was obtained with the plate oxidized at 1400°F.; the adherence obtained on the plates oxidized at 1475° to 1575°F., however, was remarkable, and in each case was comparable to the best of the ground coats. At 1600°F., the adherence was still good but was dropping off in quality; the glass-metal interface was black.

It would appear, therefore, that nickel not only retards the oxidation of iron but also has a profound effect on the nature of the oxide of iron formed. It is not safe to assume that nickel itself is involved in the adherence mechanism except as a mode of control of the amount and nature of the iron oxides formed since adherence is not obtained on pure nickel sheets.

(7) Electron-Diffraction Identification

In order to obtain a clearer picture of the nature of the oxides and metals being examined, several special preparations were subjected to electron-diffraction examination. These samples of nickel iron alloy, 36% Ni to 64% Fe (Invar), were heated for 30 seconds each in air at 1400°, 1450°, and 1500°F. Using the sodium fluoride addition, steel plates[1] were nickel flashed for 1, 5, and 15 minutes. Nonreboiling stock[1] was enameled (*a*) with zircon antimony-free vitreous enamel, applying the enamel directly to the steel without the use of ground coat and firing at 1520°F., and (*b*) a high antimony enamel, using the same procedure as (*a*).

The three samples of nickel alloy gave diffraction patterns indicating a mixture of an oxide and a metallic phase in the surface layers. The metal is either metallic Ni or a Fe-Ni alloy, differentiation being difficult, though the diffraction lines lie closer to the proper position for the Fe-Ni alloy than to pure Ni, suggesting but not proving that the alloy rather than pure Ni is present. The examination dealt with the oxide scale and not with the underlying metal, the presence of a metallic constituent being a characteristic of the scale. The oxide has a spinel structure with the lattice constant of Fe_3O_4. The identification cannot be positive owing to the similarity in structure and lattice constants of other possible materials such as $NiFe_2O_4$ and γ-Fe_2O_3. No free NiO was found, and light abrasion did not change the patterns appreciably. Section III will show that the compounds Fe_2O_3 or $NiFe_2O_4$ cannot exist in contact with metallic Ni or high Ni-content alloys under conditions of the experiment and that the oxide therefore must be Fe_3O_4.

The diffraction data indicate that metallic nickel is the material deposited in the nickel flash and both NiO and $Ni(OH)_2$ are also present but evidently in small amount. Positive identification was not clear cut, but with the data heretofore obtained, it appears certain that the coating is metallic nickel containing small amounts of the oxide or hydrated oxide of nickel, which conclusion agrees with results previously developed.

The enameled specimens developed no adherence and large areas of the glass were removed by bending the plates. The metal surface was perfectly clean and bright and exhibited no visible trace of scale. The underside of the glass plates was quite black and crystallized. The diffraction pattern obtained on the black material was the same as above, namely, Fe_3O_4, although positive identification was not possible for the reasons given previously. Since, however, all oxides except Fe_3O_4 can be eliminated in the case of Invar and since other diffraction work[7] has indicated that Fe_3O_4 is on the underside of the scale, it is safe to assume that the oxide is Fe_3O_4 and not γ-Fe_2O_3. Microscopic and magnetic observations bear out this contention. No metal was found in the under part of the scale.

The scale pattern of the nickel alloy therefore appears to be a mixture of a Fe-Ni alloy or possibly metallic Ni with Fe_3O_4; the nickel flash appears to be chiefly metallic nickel with small amounts of $Ni(OH)_2$ or NiO or both; the black oxide at the interface on a nonadhering enamel and steel appears to be Fe_3O_4 containing no admixture of metal.

III. Discussion with Particular Reference to Glass-Iron Adherence Mechanism†

A close study of the foregoing data indicates that in the last analysis the development of adherence is a con-

* See Nelson, footnote 5; Robinson, footnote 6 (*b*); and Miyake, footnote 7.

† It is outside the scope of this paper to discuss the experimental results in connection with work on enamel adherence carried out by other investigators. The reader is referred to many excellent papers and reviews on the subject in the ceramic literature.

trolled corrosion phenomenon which may be considered susceptible to examination as an oxidation-reduction equilibrium and that the equilibrium after an enamel has begun to fuse is the important part of the mechanism. On this basis, the controlling factors in development of glass-iron adherence under a particular system of time and temperature are (1) the concentration and nature of oxidizing and reducing agents plus (2) some mechanism for controlling the degree and nature of oxidation.

In view of these factors, a considerable amount of literature is available which, when examined with the experimental results already obtained, not only indicates the nature of the adherence-promoting oxide but also its mechanism of formation and thus also the mechanism of adherence development between glass and iron.

In a study of the long-time oxidation of iron at high temperatures in air, Pfeil[8] has shown that the composition of the scale is continuously variable from Fe_2O_3 to FeO, the direction of examination occurring from the outside of the scale toward and within the base iron. This general picture persists whether the scale is thick or thin, the development of scale being explained through the function of the oxides of iron as "oxygen carriers," the mechanism being one of diffusion, and the iron moving outward while the oxygen moves inward. Pfeil showed further that when FeO is heated in contact with the higher oxides of iron, a reaction takes place, forming an oxide or mixture of oxides having an oxygen content greater than required for FeO. Other workers[9] agree with Pfeil's diffusion hypothesis for oxidation of iron in hot air. Fedotiev and Petrenko[10] show that when Fe_2O_3 is first formed it reacts with the base iron to form FeO, the FeO being oxidized to a higher oxide and the reaction continues. On an absolute identity basis,[7] the exterior portions of the scale, whether thick or thin, are shown to be Fe_2O_3; and the inside portions close to the iron, Fe_3O_4.

Preoxidation of a nonboiling iron (section II (6)) does not develop or improve adherence; section II (7), showed that nonadhering enamels develop metal-free Fe_3O_4 at the metal-glass interface. On this basis, Fe_2O_3 or Fe_2O_3 in contact with Fe_3O_4 and possibly Fe_3O_4 alone cannot be the adherence-promoting oxide. In view of Pfeil's diffusion mechanism, the relative position of Fe_2O_3 in the scale is immaterial. It is evident that one of the functions of nickel flashing is the prevention or restriction of formation of Fe_2O_3 and possibly Fe_3O_4, not only in the heating-up period but also at enameling temperatures.

Only three possibilities, therefore, are left as adherence producers, namely, Fe, FeO, or Fe_3O_4 or some combination thereof.

Section (6) showed how an essentially neutral glass (a zircon enamel containing Na, K, Ca, Al, F, B, Zr, Si, and O) was fused on iron-nickel alloys. No adherence resulted, little or no oxide was formed at the interface or dissolved in the glass, and the metal surface, after the removal of the glass, was clean and bright. Not until the alloy was preoxidized was adherence obtained. This result indicates that metallic iron alone cannot be a factor in the development of adherence and that some oxide of iron must be present.

Stead[11] showed that low nickel steels oxidize first to FeO and NiO, and the metallic iron in contact immediately reduces the NiO to Ni, releasing oxygen for further oxidation of the iron. This is the picture on short-time oxidation in air. On long-time oxidation, the reaction progresses to final formation of Fe_2O_3 and NiO.[12] The compound $NiFe_2O_4$ in all probability is formed.[13] Electron-diffraction studies[7] have shown that, on long-time oxidation of nickel steels, the scale is complex with Fe_2O_3 on the outside surface and NiO underneath and that pure nickel scales to NiO. The reduction of the oxides by H_2 is shown to be facilitated by the presence of NiO or Ni.[14]

Pfeil[8] also examined the oxidation of nickel steels and showed that the process was different from that encountered for plain iron. On long-time oxidation, the heavy scales formed contained little or no nickel in the exterior portions and were chiefly iron oxides. The Ni-Fe ratio of the intermediate portions of the scale was less than that of the base metal while the portion next to the base stock exhibited a considerably higher ratio of Ni to Fe than the base metal. Nickel was present in this layer as minute particles of metal. A similar enrichment was found in stainless steel and in nickel chromium steel. Similar observations were obtained by Stead.[11] Pfeil also showed that NiO cannot remain in equilibrium with iron oxide containing more than 72% of Fe (FeO = 77% Fe), the NiO being reduced to metal under these conditions.

Pfeil, however, examined the oxides at room temperature, showing the presence of metallic Ni and Fe_3O_4. In view of Bernard,[15] who showed that at elevated temperatures NiO could exist in equilibrium with FeO and that these oxides decompose, forming Fe_3O_4 on cooling, the Pfeil limitation obviously is more properly closer to 77% Fe rather than to 72% (FeO versus Fe_3O_4) if high temperatures are considered and if the system is in contact with Fe. The oxidation mechanism of the nickel steels is still a diffusion process but it is retarded

[8] L. B. Pfeil, "Oxidation of Iron and Steel at High Temperatures," *Jour. Iron Steel Inst.*, **119** [1] 501–60 (1929).

[9] D. W. Murphy, W. P. Wood, and W. E. Jominy, "Scaling of Steel at Elevated Temperatures by Reaction with Gases and Properties of Resulting Oxides," *Trans. Amer. Soc. Steel Treating*, **19** [3] 193–225 (1932); *Chem. Abs.*, **26,** 1554 (1932).

[10] P. P. Fedotiev and T. N. Petrenko, "Mechanism of Oxidation of Iron by Steam, CO_2, and Air at High Temperatures," *Z. Anorg. Allgem. Chem.*, **157,** 165–72 (1926); *Chem. Abs.*, **21,** 366 (1927).

[11] J. E. Stead, "Notes on Nickel Steel Scale and on Reduction of Solid Nickel and Copper Oxides by Solid Iron," *Engineering*, **102,** 367–68 (1916).

[12] M. Bound and D. A. Richards, "Study of Atmospheric Oxidation of Metals and Alloys," *Proc. Roy. Soc.* [London], **51,** 256–66 (1929); *Chem. Abs.*, **33** [12] 4567 (1939).

[13] J. Longuet and H. Forestier, "Study of Rate of Reaction Between Solids Below Recrystallization Temperature," *Compt. Rend.*, **216,** 562–64 (1943); *Chem. Abs.*, **38** [10] 2259 (1944).

[14] K. Grossman and E. J. Kohlmeyer, "Reduction of Mixed Oxides," *Z. Anorg. Allgem. Chem.*, **222,** 257 (1935).

[15] J. Bernard, "Étude de la Decomposition du Protoxide de Fer et de Ses Solutions Solides," *Ann. Chim.* [Series 11], **12** [1] 5–92 (1939).

by the presence of nickel at the crystal interfaces. The nickel grains in contact with iron and iron oxide remain as metal until all iron is oxidized. The slowness of the process is due to the necessity for interdiffusion of Fe and Ni.

It is thus evident that with Ni steel, nickel alloys, or nickel-flashed steel the oxidation process at elevated temperatures must explain the presence of metallic nickel particles in the scale but close to the core. In view of Pfeil's findings on the inability of NiO to exist in contact with iron oxide having an iron content between 72 and 77% Fe, a mechanism for the formation of nickel metal in the scale becomes evident.

When the foregoing theory is examined in the light of the work of other investigators and the whole is correlated with the results of the electron-diffraction studies, a clear picture of the oxidation mechanism is available. Bernard[15] has shown that FeO formed at high temperature decomposes on cooling in accordance with the reaction

$$4FeO \longrightarrow Fe_3O_4 + Fe$$

The temperature of decomposition is 1065°F. A similar picture is shown when FeO is mixed with CoO and/or NiO. If the nickel content is high, a mixture of iron, nickel, and Fe_3O_4 is obtained at room temperature. If the nickel content is low, nickel may or may not be present. Both CoO and NiO form solid solutions with FeO, but these systems are less stable than FeO.

In the case of iron oxidized in air, it has been shown that Fe_2O_3 is first formed which reacts with the base iron by a diffusive process to form the lower oxides, the scale composition being continuously variable from Fe_2O_3 on the outside to, but possibly never reaching, FeO on the inside.

In the case of the iron-nickel alloys oxidized in air, an entirely different and opposite picture is developed, in that the lowest oxide of iron, that is, FeO, is formed first and the higher oxides of iron are formed therefrom by oxidation or thermal decomposition. The presence of Pfeil's metallic Ni close to the core after long-time oxidation at high temperatures is the result of oxidation of all of the iron in the outer oxide core to an oxide having an iron content less than 72% Fe when cold and probably less than 77% when hot, the system having been examined at a point beyond which the Bernard mechanism could be recognized. For short-time oxidation, the Bernard-Pfeil-Stead mechanisms take place in a fashion easy to recognize. On heating, both NiO and FeO form, the NiO immediately decomposing to metal and releasing oxygen either for further oxidation of Fe or for oxidation of FeO or both. On cooling, the FeO decomposes to Fe and Fe_3O_4, and since NiO will not exist as oxide in the cooling cycle with iron oxides having more than 72% Fe, nickel will also be present as metal. Owing to the ease with which Fe and Ni form solid solutions, the cold scale should consist of nickel-iron alloy mixed with Fe_3O_4, which is the picture suggested by electron diffraction; and from this picture, it appears rather doubtful that any Fe_3O_4 is formed except on cooling.

From an adherence standpoint, it has been shown that Fe_2O_3, Fe_2O_3 plus Fe_3O_4, possibly Fe_3O_4, and Fe-Ni are not in themselves adherence developers. In view of the discussion of the literature, the presence of Fe_3O_4 without admixed metal as shown at the interface of a nonadhering enamel is the result of reduction of Fe_2O_3 rather than of decomposition or oxidation of FeO. The presence of Fe_3O_4 under the enamel in the short-time firing must have been due to the development of reducing conditions.

Preoxidation of nickel alloy yielded a scale on cooling consisting of Ni + Fe + Fe_3O_4, and extraordinary adherence was obtained with a zircon enamel. The mechanism is undoubtedly as follows: The enamel-coated Ni + Fe + Fe_3O_4 remains substantially stable up to about 1000° to 1200°F., owing to the stabilizing presence of nickel, at which point the enamel starts to fuse over, shutting off external oxidation. The Bernard reaction starts to reverse itself, that is, $Fe + Fe_3O_4 \rightarrow 4FeO$. In addition, the reaction tends to be forced in the direction indicated by two forces, (*a*) the restrictive effect of the presence of Ni trying to oxidize and thus stabilizing the formation of the highest iron-containing oxide of iron and (*b*) the reducing conditions noted in the preceding paragraph.

It would thus appear that the oxide important for adherence is FeO, as free from the other oxides of iron as possible, and that the presence of metallic iron in the form of dendrites and magnetite in the cold bond may be explained through the thermal decomposition of FeO. If any substantial amount of Fe_2O_3 and Fe_3O_4 is present at enameling temperatures, adherence will not develop.

Experimental proof of the foregoing mechanism has been shown by King,[16] who measured the electrical resistance exhibited across an enamel metal interface on heating and cooling. He found that, with an enamel developing good adherence, the resistance was relatively low at enameling temperatures but very low on cooling, and he used these findings as proof of the formation of metal dendrites of iron on cooling. With a nonadhering enamel, a relatively low resistance is obtained at enameling temperatures, the resistance decreasing as the temperature is increased and increasing strongly as the enamel cools. The resistance of a nonadhering enamel at peak temperature was comparable to the resistance of a well-adhering enamel at room temperature. When the resistances of these same enamels over the temperature range were obtained on platinum, they were very much higher throughout, showing the necessity for the presence of iron. The behavior of an adhering and nonadhering enamel was comparable on platinum.

The oxides of iron are relatively poor conductors even at elevated temperatures,[17] so the low resistance results for the room-temperature, well-adhering enamel must be due to a metallic constituent (see King[16]).

These explanations indicate that the formation of dendrites is a secondary phenomenon, whereas the den-

[16] R. M. King, "Mechanics of Enamel Adherence: XIV. (1) Role of Cobalt Oxide in Metal and Oxide Precipitation During Ground-Coat Firing Cycle and (2) Determination of Temperature and Time Intervals of Precipitation," *Jour Amer. Ceram. Soc.*, **26** [2] 41–48; "XV, Influence of Cobalt and Nickel Oxides on Metal Precipitation and Ground Coating-Iron Interface," *ibid.*, [10] 358–60 (1943)

[17] International Critical Tables, Vol. VI, p. 154, 1929.

drites themselves may be the actual mechanical fingers developing the adherence. It is significant that their formation would not normally be possible without prior formation of FeO at enameling temperatures. That these dendrites are the actual grip mechanism appears to be evident in a comparison of the oxide of the underside of the nonadhering enamel and the preoxidized coating on the nickel alloy. Both surfaces show Fe_3O_4 at room temperature. In the adherence scale, however, metal is present; in the nonadherence scale, no metal is present. A well-adhering bond, in addition, should show the presence or the effect of the presence of a stabilizing agent, such as Ni, which insures the formation of FeO at high temperatures.

This discussion indicates that the material important for adherence at enameling temperatures is FeO, and a mechanism for its formation for effectiveness in the adherence mechanism has been shown in the case of nickel alloys.

Several possibilities exist for the oxidation of iron in the enameling cycle: (1) O_2, CO_2, and/or H_2O from the external atmosphere, (2) CO_2 and/or H_2O from the enamel system, and (3) an oxygen or oxidation agent as a result of easily reducible ingredients in the enamel.

As shown previously, the direct oxidation of iron before enamel fusion and without restrictive mechanisms results in the formation of oxides useless for adherence purposes. This type of oxidation is to be avoided as much as possible. After the enamel has begun to fuse, small amounts of CO_2 or H_2O or both may be evolved by the system. Under equilibrium conditions, these gases normally oxidize iron to FeO.[18] In the absence of a controlling mechanism, the oxidation will proceed to the higher oxides. In the absence of a controlling mechanism but after the enamel has fused, the H_2 and CO formed by oxidation of Fe to FeO with H_2O and CO_2 will reduce any higher oxides already formed to Fe_3O_4 because the oxygen supply has been shut off by fusion of the enamel. This mechanism evidently explains the rapid formation of Fe_3O_4 under a nonadhering enamel at the interface, the reaction of Fe plus Fe_2O_3 after the oxygen supply is shut off heading in the same direction. Thus, the presence of H_2O or CO_2 or both will aid in the formation of the lower oxides of iron, but under the conditions they cannot be solely responsible for the development of good adherence.

The only oxidation, therefore, that can be effective for adherence purposes is No. (3), in the possibilities for iron oxidation in the enameling cycle, in which the oxidation of the base iron is obtained from the decomposition of easily reducible ingredients in the enamel.

For enamels which develop adherence but which do not contain nickel, therefore, a simple explanation is available in view of the results with the Ni-Fe alloy. Such enamels will contain oxides reducible at enameling temperatures. On fusion in contact with iron, these are possibly reduced to a lower oxide but more probably to metal; FeO results from such oxidation, and in the presence of the reduced residue of the original easily reducible oxide acts as a stabilizing medium for FeO or even for the reduction of Fe_3O_4 to FeO. Such residues act in exactly the same fashion as metallic nickel. Such residues, moreover, would also have a temperature and oxygen pressure condition at which they could not exist in contact with an oxide of iron having less than 72% iron at room temperature.

There is a good possibility that for the best adherence the residue from the easily reducible oxide should combine or alloy with the dendritic Fe precipitating out since this reaction apparently occurred in the case of the Ni-Fe alloy. Materials which may be suitable for adherence purposes may be as follows: oxides of Cu, Ag, Zn, Sn, Pb, V, As, Sb, Bi, Cr, Mo, W, Mn, Co, Ni, alone or in combination. Whether or not any one or any combination of these oxides will be effective at enameling temperatures will depend on (*a*) the nature of the oxide-glass equilibria existing at enameling temperatures, particularly those in contact with iron,[19] (*b*) on the general oxidation-reduction equilibrium conditions which are available at enamel temperatures in their presence, and possibly (*c*) whether the reduced residue is a metal which can alloy with iron.

These adherence materials may be supplied or made to function in one of three ways or in combinations thereof, namely, (1) through the composition of the metal being enameled (Ni-Fe alloy), (2) through the use of an added surface (Ni flashing), or (3) through the enamel composition.

Examples of (1) and (2) have been discussed. In order that the materials in the silicate system may act as adherence promoters or developers, at least the following four requirements should be fulfilled: (*a*) In a silicate system, this reaction should be possible

[18] (*a*) J. B. Austin and M. J. Day, "Chemical Equilibrium and Control of Furnace Atmosphere," *Ind. Eng. Chem.*, **33** [1] 23–31 (1941); *Ceram. Abs.*, **20** [3] 76 (1941).

(*b*) D. P. Bogatskiĭ, "Reduction of Nickel Oxides with H_2," *Metallurg*, **12** [4] 58–65; "Reaction of Nickel Oxides with H_2 and Water Vapor," *ibid.*, **12** [7] 90–97 (1937).

(*c*) A. Krupkowski and J. Jaszczurowski, "Rate of Oxidation of Metals at High Temperatures," *Congr. intern. mines mét. géol. appl. 7e Session, Paris, Oct., 1935, Mét.*, **2**, 329–36; *Chem. Abs.*, **30**, 8115 (1936).

(*d*) L. Wohler and O. Balz, "Determination of Valence Scale of Fe, Co, Ni, Cu, Mn, Sn, and W by Means of Water-Vapor Equilibrium, and Dissociation Pressure of Oxides of These Metals," *Z. Electrochem.*, **27**, 206–19 (1921); *Chem. Abs.*, **16**, 192 (1922).

(*e*) Adam Skapski and Joseph Dabrowski, "Equilibrium and Heat of Reaction of $NiO + H_2O = Ni + H_2O$," *Z. Electrochem.*, **38**, 365–70 (1932); *Chem. Abs.*, **26** [17] 4527 (1932).

[19] (*a*) H. zur Strassen, "Equilibrium Among Fe, Ni, and Their Silicates in State of Fusion," *Z. Anorg. Allgem. Chem.*, **191**, 209–45 (1930); *Chem. Abs.*, **24**, 5581 (1930).

(*b*) W. Jander and H. Senf, "Dependence of Equilibrium $FeO + Ni \leftrightarrows NiO + Fe$ in Melt with SiO_2 Additions: III, Communication on Equilibrium Between Metal, Sulfides, and Melt," *Z. Anorg. Allgem. Chem.*, **217** [1] 48–52 (1934); *Ceram. Abs.*, **14** [4] 101 (1925).

(*c*) J. A. Hedvall and G. Schiller, "Increased Velocity Formation in Silicates of Powdered Mixtures," *Z. Anorg. Allgem. Chem.*, **221**, 97–102 (1934); *Chem. Abs.*, **29** [8] 2429 (1935).

(*d*) P. Bardenheuer and E. Brauns, "Equilibrium Between Iron and Nickel and Their Silica-Saturated Silicates," *Mitt. Kaiser-Wilhelm Inst. Eisenforschung*, **17** [9] 127–32 (1935); *Ceram. Abs.*, **15** [1] 9 (1936).

$Fe + MSiO_3 \leftrightarrows FeSiO_3 + M$; it will be noted that metallic iron is one of the reactants and that ferrous iron is one of the end products; (*b*) reaction (*a*) should take place under the general conditions existing at enameling temperatures and to a useful extent; (*c*) the formation of M should stabilize the presence of FeO and should insure its continued development between iron and the glass system under enameling conditions; (*d*) it may be necessary (but not provable at this writing) that, for best results, Fe and M should be capable of combining or alloying.

IV. Summary of Discussion

The adherence-promoting oxide for sheet steel appears to be FeO at enameling temperatures. At enameling temperatures, FeO is formed under certain equilibrium conditions which are obtained through the presence or formation of a material, probably a metal taken from the group of materials known as adherence promoters, which acts as a stabilizer for and the continued development of FeO.

The bond at room temperature will consist of a mixture of the stabilizer material, probably metal, metallic iron, and Fe_3O_4, the last two the result of decomposition of FeO on cooling; an alloy of iron and the stabilizing metal possibly may form.

The adherence promoters in the glass must meet certain equilibrium conditions to be effective, and they may operate singly or in combination. In the bond, Fe_2O_3 alone or in combination with the other oxides, or Fe_3O_4, in the absence of metal are not developers of adherence; they may develop adherence, however, if such conditions exist at enameling temperatures; and adherence will develop certainly if the room-temperature conditions indicate their presence.

Acknowledgment

The authors wish to acknowledge the assistance of W. A. Wesley, Assistant Director of Research, International Nickel Co., Research Laboratories, Bayonne, N. J., who supplied the samples of Invar metal and the bright annealed nickel-flashed specimens; for an illuminating discussion and correspondence relative to nickel flashing and equilibria conditions of nickel at high temperatures; and for permission to refer to portions of the paper by Wesley and Copson (see footnote 2 (*q*)).

The electron-diffraction data were obtained by H. R. Nelson, C. M. Schwartz, and D. Vaughn of Battelle Memorial Institute, Columbus, Ohio.

The authors are particularly indebted to staff members of the Titanium Alloy Mfg. Co.; to G. F. Comstock, chief metallurgist, and his assistant, A. Yacco, for preparation of the photomicrographs on the nickel-flashed specimens; to C. A. Best, chief chemist, and his staff, for numerous nickel determinations; and to J. Milek, who worked out the section of heating of the nickel-flashed specimens in air on a quantitative basis.

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DETERMINATION OF REFLECTANCE OF WHITE ENAMEL FRITS BY TURBIDITY METHOD*

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Abstract

A method for the determination of the reflectance of powdered frits is described. Results obtained by this method show a high correlation with the results of standard reflectance tests, particularly when frits are fused at enameling temperatures.

The method consists essentially of suspending 0.4 cc. of sample, sized between 270- and 325-mesh, in 10 cc. of clear kerosene and measuring by means of a photoelectric cell the decrease in light transmitted as compared with the light transmitted by kerosene itself. The Cenco-Sheard-Sanford photelometer was used for these measurements.

I. Introduction

During the past fifteen years, measurement of the reflectance of enameled surfaces has become essential and has also become so simplified and so well known that a detailed discussion and documentation of this subject seems unnecessary. A method of measuring the reflectance of the granular frit itself, however, has not been developed. Such measurements are sometimes desirable in order to determine the effectiveness of the frit opacifying agent, the influence of melting time and temperature on frit reflectance, and the contribution of firing and the various mill additions to the surface reflectance as determined by standard reflectance methods. It has been the object of this investigation to develop a method for this purpose.

II. Experimental Studies

Nephelometric or turbidometric methods have been used for the determination of particle size in the subsieve range. Wagner[1] and States[2] have used such methods for studies on the fineness of Portland cement.

* Forty-Seventh Annual Program, The American Ceramic Society, 1945 (Enamel Division, No. 5). Received April 28, 1945 (revised copy received August 12, (1945).

[1] L. A. Wagner, "Rapid Method for Determination of Specific Surface of Portland Cements," *Proc. Amer. Soc. Testing Mat.*, **33** [Part II] 553 (1933).

[2] M. N. States, "Specific Surface and Particle-Size Distribution of Finely Divided Materials," *ibid.*, **39**, 795–809 (1939); *Ceram Abs.*, **19** [8] 195 (1940).

TABLE I

SUMMARY OF EXPERIMENTAL DATA

No.	Frit	Density	Ground frit reflectance: Frit	Ground frit reflectance: Fused frit	Ground frit reflectance: Frit + 6% clay (fused)	Standard plate reflectance
1	Low opacity	2.57	32	54	44	29
2	" "	2.66	68	73	71	60
3	" "	2.55	33	41	43	23
4	Medium opacity	2.64	69	70	70	61
5	Normal opacity	2.69	79	73	75	69
6	Medium antimony	2.69	77	73	78	63
7	Superopaque	2.69	75	73	74	66
8	"	2.73	75	77	76	72
9	High antimony	2.72	77	77	78	72
10	Zircon	2.70	47	73	73	69
11	"	2.73	47	74	75	77
12	"	2.75	46	77	81	77
Avg.			60	70	70	62

Correlation coefficients (for explanation, see p. 328)

Frit to plate reflectance	0.58
Same with zircon frits omitted from calculation	0.915
Frit (fused at 1500°F.) to plate reflectance	0.965
Frit + clay (fused at 1500°F.) to plate reflectance	0.975

Insofar as is known this principle has not been employed in evaluating the relative opacity of enamel frits. It is based on the Beer-Lambert law which may be expressed by formula (1).

$$\text{Log } I - \log I_o = -ElC \qquad (1)$$

I_o = initial intensity of transmitted light, I.
I = intensity of light transmitted through l cm. of medium whose light-absorbing constituent has concentration, C.
E = a constant.

States[2] has modified this relationship for a suspension of small particles which presumably do not transmit light and has expressed it as follows in formula (2).

$$S_d = -c \log I_o - \log I_d \qquad (2)$$

S_d = surface area (sq. cm.) of all particles smaller than $d\mu$.
c = proportionality factor assumed constant for all concentrations whose transmissions lie within moderately limited range near unity and for all particle sizes.
I_o = intensity of light transmitted by dispersing medium when no particles are present.
I_d = instantaneous value of transmitted light intensity at time all particles greater than $d\mu$ have settled below the reference level.

For the purposes of this investigation, it was decided to keep S_d practically constant by screening the sample through a 270-mesh sieve and retaining on a 325-mesh sieve thus obtaining an approximately uniform particle size. The amount of sample added was 0.4 cc. in all determinations and hence c was assumed constant. I_d was measured for the assumed conditions that all particles transmitted some light and that $I_o - I_d$ was proportional to the light-reflecting powers of the enamel frit. These assumptions were tested by means of correlation coefficients calculated from the experimental data.

A Cenco-Sheard-Sanford photelometer, whose general design is shown in Fig. 1, was employed for these measurements. The sample was placed in 10 cm. of clear white kerosene measured into a special glass cell.

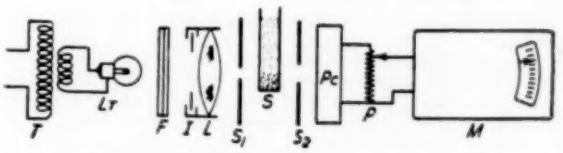

FIG. 1.—Schematic diagram of photelometer arranged for fineness measurements (courtesy American Society for Testing Materials).

The microammeter, M, was set at 100 scale divisions with a similar cell containing clear kerosene only in position S; this is called the calibrating cell. The cell containing the sample was shaken for about one minute and quickly placed in a sliding cell holder and shifted to position S. A reading was taken as soon as the pointer came to rest. The calibrating cell was then returned to the transmitting position and the indicator again adjusted to 100 scale divisions. These operations were repeated until six readings on a single sample were obtained. Samples were duplicated by separate grindings in order to determine the variations of light transmission caused by possible differences in grain size arising from sample preparation. The average of the twelve readings on two samples was subtracted from 100 and the difference recorded as the ground frit reflectance.

The samples were screened carefully in order to avoid retention of an excessive amount of fines. As a check against this, however, readings on no sample were used if after settling two minutes the microammeter reading was less than 90. Thus no more than ten scale divisions were represented in the light-obstructing power of the suspended fines. Reasonably good reproduction of readings was obtained when this procedure was employed. The average deviation of observations was about 0.50 scale division and that for the duplicate sample and arising from differences in sample

preparation was about 0.60, thus giving a total average deviation of 1.10 scale divisions.

III. Data

Pertinent data and correlation coefficients are given in Table I.

A correlation coefficient may be defined as a measure of the approach to a straight-line interrelationship between two variables. Thus if the values are plotted from one column under "ground frit reflectance" and the values under "standard plate reflectance," the points obtained would be grouped in some fashion about a straight line. If they lie in a true straight line in the upper right and lower left quadrants, the coefficient is $+1$; if the points have a circular distribution, the coefficient is zero; if they form a straight line in the other quadrants, the coefficient is -1. Other groupings would be elliptical in form.

A high positive coefficient indicates that high values of one variable are associated with high values of the other and low values of one with low values of the other. A coefficient of zero indicates no interrelationship between two variables. If the coefficient is negative the relationship is inverse.

Knowledge of the magnitude of one does not lead to any knowledge of the magnitude of the other, but a coefficient of unity means that when the value of one character is known the other is fully defined. Values between 0 and 1 indicate degrees of intensity of association between variables.

A correlation coefficient should not be considered to be a measure of causal dependence, that is, that one is the absolute cause of the other, but rather it should be considered as a mathematical expression for the degree of association between variables. A high coefficient suggests the probability of a cause and effect relationship between the two variables, but it may indicate only that two different phenomena arise from a common cause.

From data published in 1918, a correlation coefficient of 0.98 was found between total salaries paid school superintendents and teachers and the total consumption of liquor in the United States over a period of years. No functional relationship could be proved nor could one seriously be argued, but such a relationship could easily arise from a common cause—prosperity or a lack thereof.

A mathematical expression for the calculation of correlation coefficients is shown by equation (3).

$$r_{xy} = \frac{\frac{\Sigma xy}{n} - \bar{x}\,\bar{y}}{\sigma_x\,\sigma_y} \qquad (3)$$

x and y represent the individual pairs of values.
n = number of pairs.
$\bar{x}$ and $\bar{y}$ = avg. of x and y values, respectively.
σ_x and σ_y = standard deviations for x and y values.

(1) Discussion of Data

The nature of the samples is indicated by the second column (type of frit), and it will be noted that four general types of frit were tested as supplied by three manufacturers.

Keeping in mind that the value of correlation coefficients ranges from -1 to $+1$, it will be seen that the significance of the data is included within the calculated coefficients. The correlation between frit reflectance and standard plate reflectance is poor if the values for the zircon frits are included but excellent if these are omitted from the calculations. When the frit is fused at 1500°F., the correlation is better; and when fused at 1500°F. with 6% Vallendar clay, the correlation is still better.

The opacity in all frits was increased by simply fusing at usual firing temperatures. The increase for the zircon enamels was marked. The reflectance of most enamels was not changed markedly by the addition of clay. The greatest change was that of enamel No. 1, which was reduced from 54 to 44. The averages for the fused frits and fused frit and clay mixtures were the same.

It will be noted that the reflectance of the fused mixtures, which should most logically be compared with plate reflectance, ranges from two scale divisions lower to 20 scale divisions higher than the plate reflectance.

IV. Conclusions

When the zircon frits were not included there was a high correlation between frit reflectance as determined by the method described in this investigation and the standard plate reflectance. Therefore, one can be reasonably sure that individual values in a series of frit reflectance values will bear the same relation to each other as the values for these same frits in a series of standard plate reflectance values. That is, any factor influencing the reflectance of the frit itself will influence the standard reflectance in a similar manner. A greater certainty for this relation will be obtained if the frit is fused at 1500°F., and a still greater certainty will be obtained if the frit is fused with 6% of the clay used for the standard reflectance.

The data presented herein indicate that the clay used contributes very little opacity to the enamel.

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